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Ionic Liquid Modified Carbon Nanotube Supported Palladium Nanoparticles for Efficient Sonogashira-Hagihara Reaction

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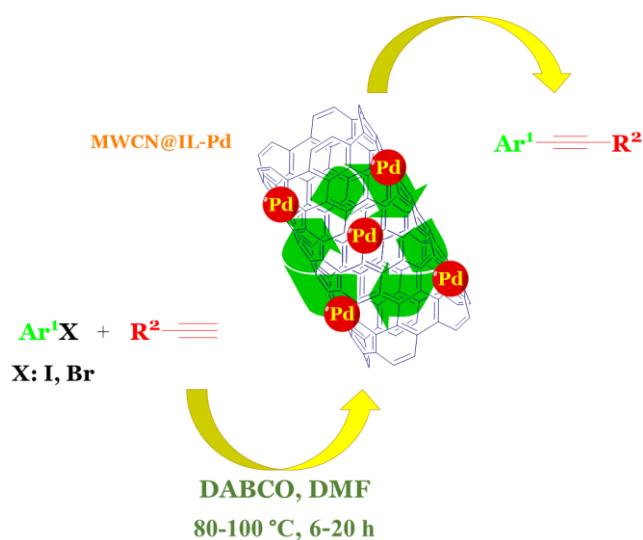
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Highlights

- A Pd NPs supported onto an ionic liquid-modified carbon nanotube is prepared and characterized.
- The new Pd catalyst applied efficiently in copper-free Sonogashira-Hagihara reaction.
- This heterogeneous catalyst is recycled for 5 runs maintaining its efficiency.

Graphical Abstract



Abstract

A Palladium supported onto an ionic liquid-modified carbon nanotube is prepared. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), thermogravimetric analysis (TGA), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) are used to complete its characterization. The application as catalyst in the copper-free Sonogashira-Hagihara coupling is also studied employing different substrates. This heterogeneous catalyst is successfully recycled for 5 consecutive identical reactions maintaining its efficiency. After this fifth catalytic run the catalyst is characterized again.

Keywords: MWNTs, Sonogashira-Hagihara, Copper-free, Ionic liquid, Palladium

1. Introduction

Nowadays, novel nanosized catalysts, having high surface area, produce excellent catalytic activity. Their recovery and recycling with minor leaching of active species and deactivation, are interesting features to study [1,2]. Apart from all different supports used in the preparation of heterogeneous catalysts, carbon nanotubes (CNTs), which have high surface areas, high thermal and chemical stabilities and excellent mechanical strengths, have received an enormous attention. In fact, many organic transformations involving this strategy have been published [3,4]. Particularly, the surfaces of CNTs can be modified with several phosphorous or nitrogenous ligands, or ionic liquids (ILs), resulting suitable sites for stabilization of catalytically active metal nanoparticles. ILs having excellent properties such as a wide temperature range over the liquid phase, high thermal stability, strong interaction with active metals, non-volatility and non-flammability, enable to dissolve polar organic compounds, are considered as green solvents, catalysts and reagents [5-8]. However, due to the high price of ILs, their use as a solvents are not advisable. Alternatively, the surface functionalization of solid supports with ILs structures allows organic transformations with the minimum amount of ILs [9]. Along this lone, recently special attention has been paid to using nitrogen-rich ionic liquids in different transformations [10-12].

The palladium-promoted Sonogashira-Hagihara reaction is a coupling reaction of aryl or alkenyl halides or triflates with terminal alkynes in the presence or in the absence of copper co-catalyst obtaining aryl alkynes. A large series of these compounds are important precursors for natural products, pharmaceuticals, pesticides, herbicides, etc. [13-15]. In recent years, many homogeneous and heterogeneous palladium catalysts have been reported for this specific coupling reaction [16-31].

However, the bibliographic search reveals that there are few reports concerning the employment of palladium-supported carbon nanotubes as heterogeneous catalyst in C-C coupling reactions [32-40], and more specifically in the Sonogashira-Hagihara reaction [41-46]. So, in this work, the synthesis of functionalized multi-wall carbon nanotubes (MWCNTs) with imidazolium and DABCO derived ionic liquids and triazole moieties, and their application as recyclable catalyst in the Sonogashira-Hagihara reaction are reported.

2. Experimental

2.1. Synthesis of 3-(prop-2-yn-1-yl)-1-vinyl-1H-3 λ^4 -imidazol-1-ium bromide (IL1):

1-Vinylimidazole (6 mmol, 0.54 mL) and propargyl bromide (9 mmol, 0.65 mL) were added to a flask containing dry acetone (6 mL) and the resulting mixture was stirred at 40 °C for 24 h under an argon atmosphere. The acetone was evaporated and the resulting solid was washed with hexane (3 \times 10 mL) and dried at 60 °C in an oven for 24 h. Pure white 3-(prop-2-yn-1-yl)-1-vinyl-1H-3 λ^4 -imidazol-1-ium bromide was obtained in 83% isolated yield and characterized by ^1H and ^{13}C NMR spectra.

2.2. Synthesis of 1-(2-bromoethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium bromide [DABCO-bromoethane][Br] (IL2):

1,4-Diazabicyclo[2.2.2]octane (DABCO) (5 mmol, 0.56 g) was dissolved in dry THF (10 mL) and the mixture was cooled to 0 °C in an ice bath. Then, 1,2-dibromoethane (25 mmol, 2.1 mL) was added and the reaction mixture was stirred for 24 h at room temperature. Then, THF was evaporated and the obtained white solid was washed with hexane (3 \times 10 mL) and dried at 60 °C in an oven for 24 h. Pure 1-(2-bromoethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium bromide was obtained in 92% isolated yield and characterized by ^1H NMR spectra.

2.3. Synthesis of 1-(2-(4-((3-vinyl-1H-3 λ^4 -imidazol-1-ium-1-yl)methyl)-1H-1,2,3-triazol-1-yl)ethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium bromide (IL3):

Initially, [DABCO-bromoethane][Br] (5 mmol, 1.5 g) (IL2) and sodium azide (7.5 mmol, 0.48 g) were added to a flask containing deionized water (4 mL) and the reaction mixture was stirred for 24 h at 50 °C. Afterwards, to the resulting mixture, ionic liquid IL1 (5 mmol, 1.1 g), ascorbic acid (0.21 mmol, 36 mg) and copper(II) sulfate pentahydrate (0.06 mmol, 15 mg) were added and the mixture was stirred at 50 °C for 24 h. Finally, solvent was evaporated until 1 mL of solution remained and,

then, 5 mL ethanol was added. The resulting solid was separated by filtration, washed with ethyl acetate (3×10 mL), and dried at 40 °C in a vacuum oven for 48 h.

2.4. Preparation of multi-wall carbon nanotubes functionalized with the hydroxyl group:

Multi-wall carbon nanotubes (MWCNTs) having the hydroxyl functional group were prepared following the procedure described in the literature [47]. MWCNTs (2 g) were added to a flask containing 30% H₂O₂ (40 mL) and the reaction mixture was sonicated for 10 min at room temperature. Then, the resulting mixture was stirred for 6 days at 65 °C. H₂O₂ (15 mL) was added to the reaction mixture every day. Finally, the MWCNTs functionalized with hydroxyl groups were separated by centrifugation and the obtained black solid was washed with deionized H₂O (2×15 mL) and EtOH (3×15 mL) and dried at 80 °C in an oven for 24 h. Finally, 2.2 g of freshly hydroxyl functionalized MWNTs were isolated.

2.5. Preparation of MWCNT@OH functionalized with the thiol group:

Dry toluene (15 ml) was added to a flask containing MWCNTs functionalized with the hydroxyl group (MWCNT@OH) (1 g) under argon atmosphere and the reaction mixture was sonicated for 10 min at room temperature. Then, (3-mercaptopropyl)trimethoxysilane (5 mmol, 0.9 mL) was added and the resulting mixture was stirred for 24 h at 100 °C under an argon atmosphere. Finally, the MWCNT@OH functionalized with the thiol group was separated with centrifugation and the obtained black solid was washed with absolute ethanol (2×15 mL) and dried at 80 °C in an oven for 24 h. Finally, 1.06 g of freshly functionalized MWCNTs were isolated.

2.6. Preparation of multi-wall carbon nanotubes incorporating ionic liquid 3 (IL3):

Multi-wall carbon nanotubes functionalized with the thiol group (0.8 g) and ionic liquid **IL3** (2.5 mmol, 1.2 g) were added to a flask containing methanol (30 mL) and the reaction mixture was sonicated for 10 min at room temperature. The resulting mixture was purged with argon for 30 min under argon protection. In another flask, 2,2'-azobisisobutyronitrile (AIBN) (0.12 mmol, 20 mg) was dissolved in methanol (5 mL) and purged with argon for 30 min. Finally, the solution of AIBN was added dropwise to the reaction mixture of multi-wall carbon nanotubes functionalized with the thiol group and ionic liquid **IL3** and the resulting mixture was stirred for 48 h at 70 °C under argon atmosphere. Then, the solid was separated by centrifugation and washed with H₂O (2×15) and ethanol (2×15 mL) and dried at 80 °C in an oven for 24 h, achieving 1.3 g of the new grafted material. Using CHNS analysis amount of sulphur and nitrogen were found to be 1.3% and 1.47%, respectively.

2.7. Preparation of palladium nanoparticles deposited on MWCNT@IL:

Supported **IL3** multi-wall carbon nanotubes (0.5 g) were added to a flask containing deionized water (5 mL) and the reaction mixture was sonicated for 10 min at room temperature. Then, a solution of Na_2PdCl_4 (0.035 mmol, 10 mg) in deionized water (2 mL) was added. Afterwards, an aqueous solution of NaBH_4 (1 mmol, 38 mg) in deionized water (0.5 mL) was slowly added and the final mixture was stirred for 24 h at room temperature under an argon atmosphere. Finally, the suspension was subjected to centrifugation and the obtained black solid was washed with EtOH (2×15 mL) and dried at 80 °C in an oven for 24 h, achieving 0.48 g of the final functionalized MWCNT.

2.10. General procedure for the Sonogashira-Hagihara reaction:

To a flask containing the aryl halide (0.5 mmol) and phenylacetylene (0.75 mmol, 0.08 mL), DABCO (0.75 mmol, 0.08 g) and DMF (2 mL), MWCNT@IL-Pd nanocatalyst (25 mg containing 0.5 mol% Pd) were added. The mixture was stirred at 80 °C for aryl iodides and 100 °C for aryl bromides under an argon atmosphere. After completion of the reaction (monitored by GC), deionized water (2 mL) was added to the reaction mixture and the crude product was extracted with ethyl acetate (3×5 mL). For further purification, the organic solvent was removed under vacuum and the resulting residue was purified by column chromatography on silica gel using hexane and ethyl acetate as eluents.

2.11. General procedure for the recycling of the MWCNT@IL-Pd in the Sonogashira-Hagihara coupling between iodobenzene and phenylacetylene

Iodobenzene (0.5 mmol), phenylacetylene (0.75 mmol, 0.08 mL), DABCO (0.75 mmol, 0.08 g), DMF (2 mL), and MWCNT@IL-Pd nanocatalyst (25 mg containing 0.5 mol% Pd) were added to a 5 mL flask and the mixture was stirred at 80 °C for 6 h under an argon atmosphere. After completing the reaction, the catalyst was separated by centrifugation and, after washing with ethyl acetate and drying, was utilized in the next run. This catalyst recycling was repeated up to five successive cycles exhibiting the same catalytic activity.

2.12. General method for performing the PVPy test in Sonogashira-Hagihara coupling reaction of iodobenzene with phenylacetylene

In a 5 mL flask, iodobenzene (0.5 mmol) and phenylacetylene (0.75 mmol, 0.08 mL), DABCO (0.75 mmol, 0.08 g), DMF (2 mL), MWCNT@IL-Pd catalyst (0.5 mol% Pd, 25 mg), and PVPy (200 mg) were added. The mixture was stirred at 80 °C during 6 h under argon atmosphere. Next, deionized water (2 mL) was added to the reaction mixture, crude product extracted with ethyl acetate and progress of the reaction was monitored by GC.

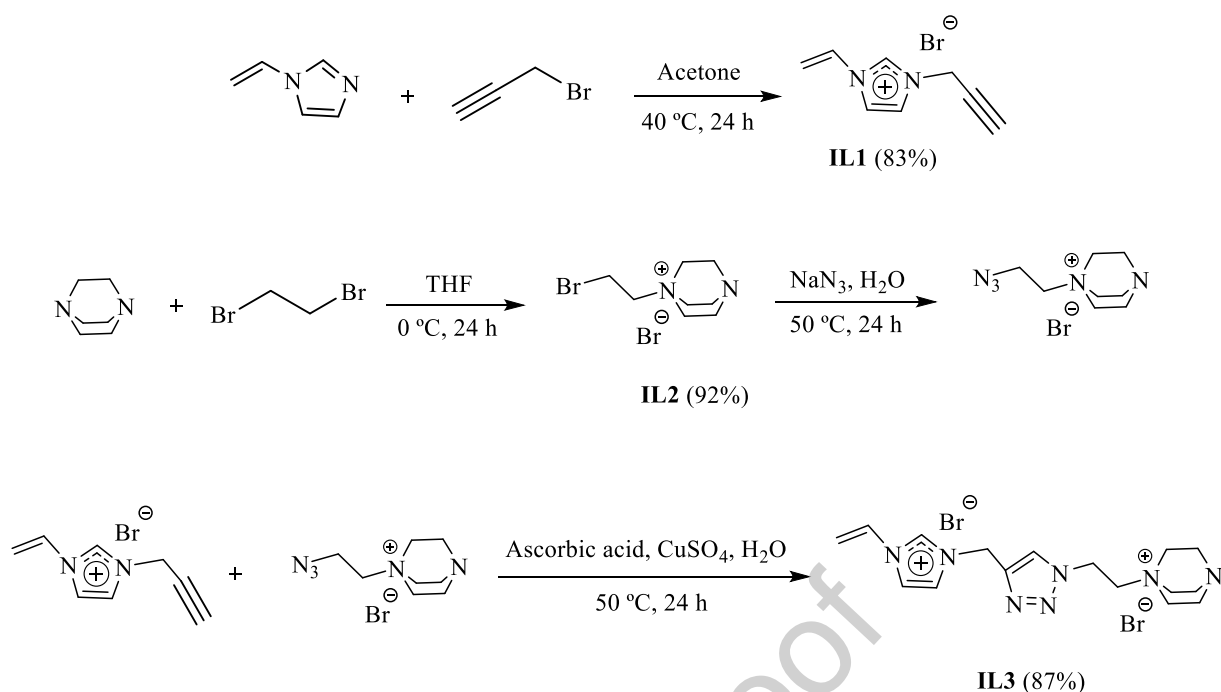
2.13. General method for performing the TGA analysis of MWCNT@IL3 and CNT-OH catalysts

Firstly, the desired method was introduced controlling the temperature and atmosphere nature for performing the analysis (25-700 °C, O₂ atmosphere) and then, the special crucible of TGA analysis was adapted in the device and its weight set onto zero. Next, 5-7 mg of MWCNT@IL3 were added in the crucible and transferred to the thermobalance device. After that, the desired method was run for performing the analysis. The same procedure was repeated for performing the analysis of the CNT-OH sample.

3. Results and discussions

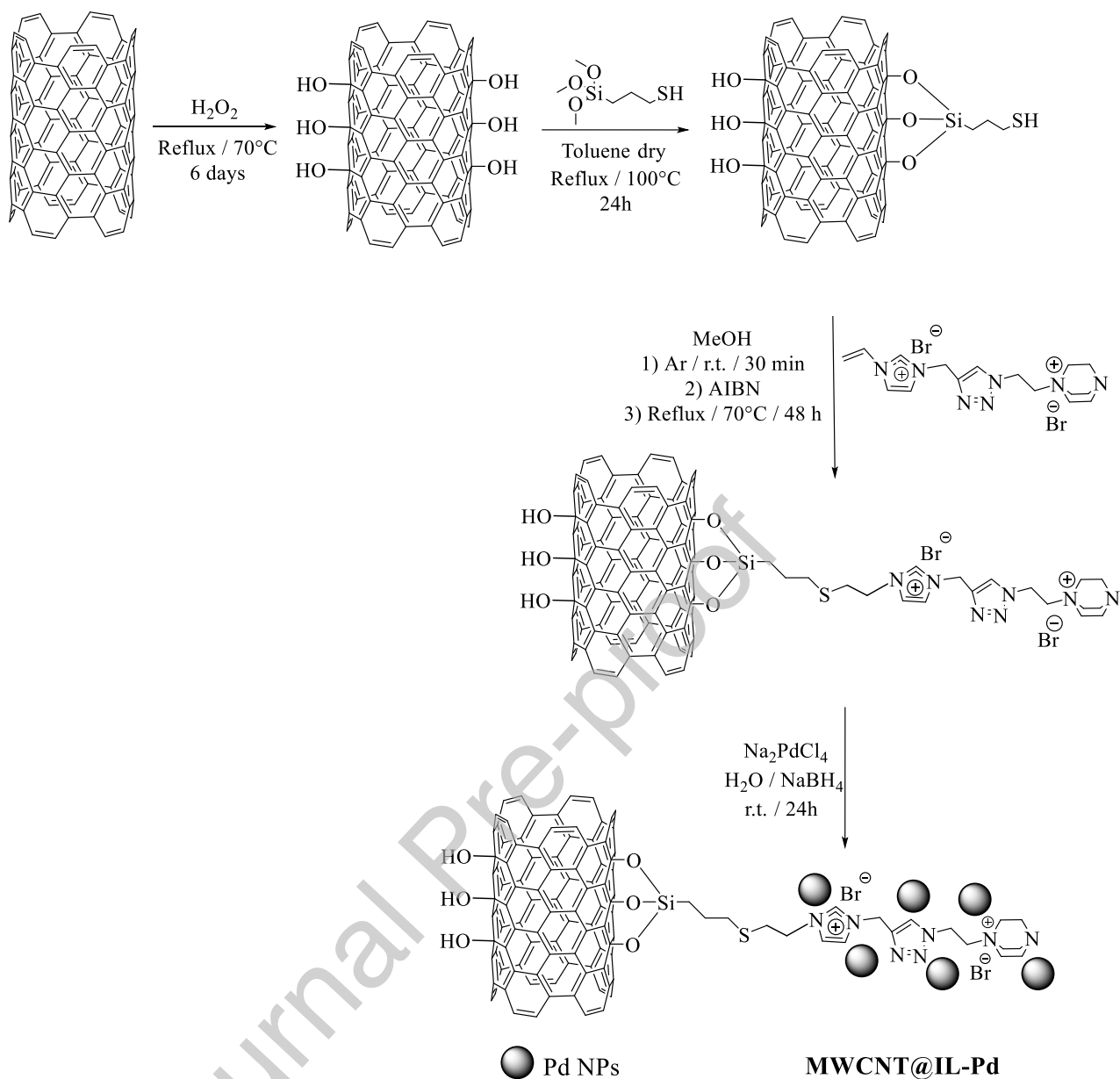
3.1. Materials and characterization

For preparation of the **IL3**, initially 1-vinylimidazole was allowed to react with propargyl bromide in acetone affording **IL1**. In a parallel way, **IL2** was obtained after reaction of DABCO with 1,2-dibromoethane at 0 °C. After azidation of **IL2**, the non-characterized azide and **IL1** were the components of a 1,3-dipolar cycloaddition mediated by ascorbic acid (AAC) and copper(II) sulfate, affording **IL3** in 87% isolated yield (Scheme 1).



Scheme 1: Preparation steps of the **IL3**

In order to prepare the palladium supported catalyst, MWCNTs were treated with H_2O_2 producing hydroxylated MWCNTs, which was reacted with (3-mercaptopropyl)trimethoxysilane to introduce the thiol group. Then, the resulting thiol functionalized MWCNTs were reacted with **IL3** under thiol-ene reaction conditions. Afterwards, IL modified MWCNTs were allowed to react with Na_2PdCl_4 followed by reduction with NaBH_4 (Scheme 2). The final composite will be referred as MWCNT@IL-Pd throughout the text of this article (Scheme 2). The amount of palladium in MWCNT@IL-Pd was $0.11 \text{ mmol}\cdot\text{g}^{-1}$, which was determined by atomic absorption spectroscopy (ASS).



Scheme 2: Preparation of the MWCNT@IL-Pd catalyst

The presence of different elements such as N, C, S, Br, and Pd in the structure of MWCNT@IL-Pd was confirmed using energy dispersive X-ray analysis (EDX). The presence of iron atom is due to the use of this element as a catalyst during the synthesis of CNTs [48-49] (Figure 1).

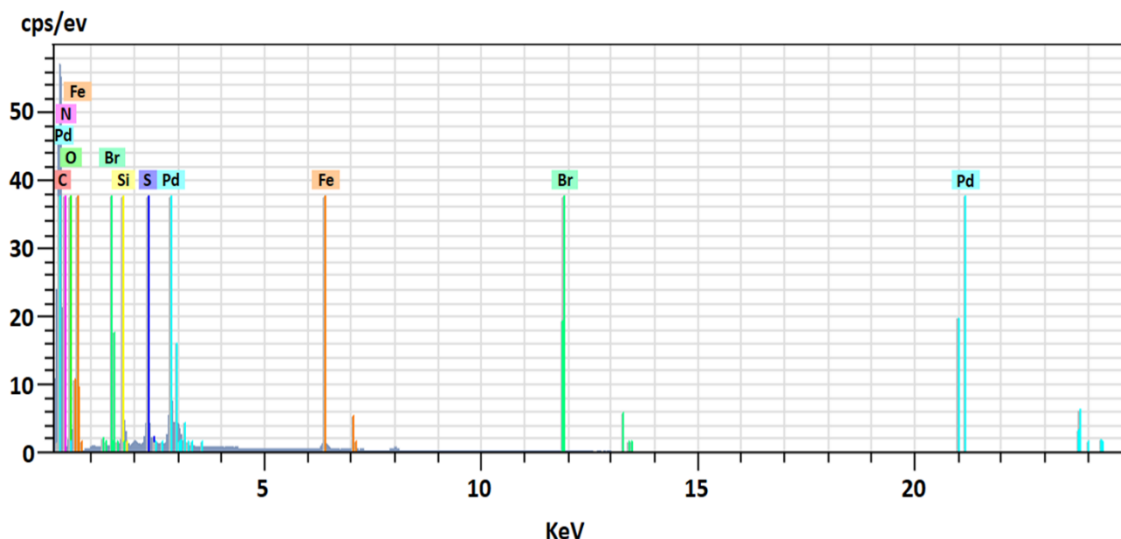


Figure 1: EDX spectrum of MWCNT@IL-Pd

SEM-Map image of MWCNT@IL-Pd showed very uniform distribution of Pd particles in the structure (Figure 2).

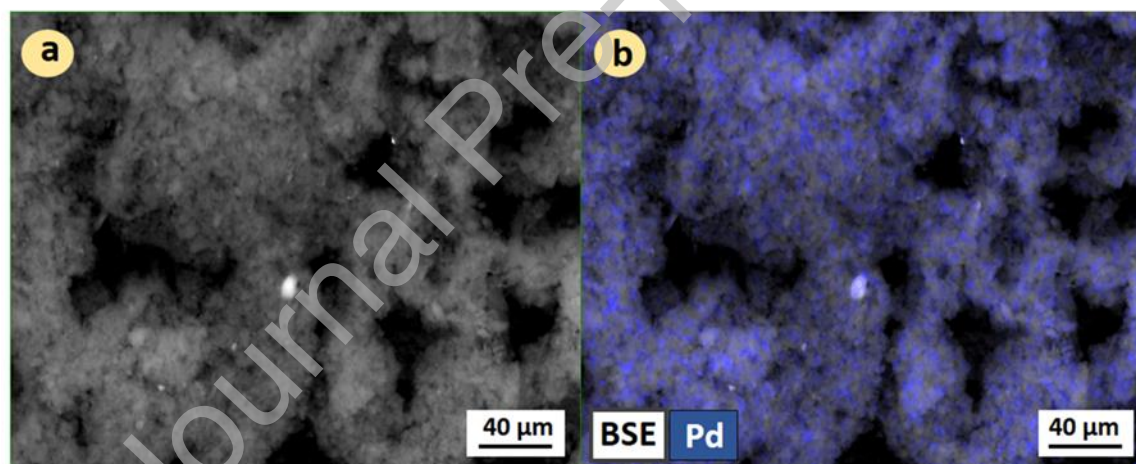


Figure 2: a) SEM and b) map image of Pd in MWCNT@IL-Pd

Also, XRD analysis of MWCNT@IL-Pd is showed in Figure S1. The peak appeared at 25.7 is related to the hexagonal carbon structure of CNTs in the (002) plane. However, Pd(0) pattern did not appear in the XRD because the palladium content in the supported material is less than 3-5% [50].

X-ray photoelectron spectroscopy (XPS) in C, Si, S, N, Br, and Pd regions were studied (Figure 3). The C 1s XPS spectrum for the MWCNT@IL-Pd showed four peaks centered at 284.5, 285.4, 286.4, 287.6, which are related to C=C, C-C, C-O, and C=O arrangements, respectively (Figure 3a) [51,52]. As it can be seen in Figure 3b, XPS spectra in Si 2p region showed two main peaks located at 102.1 and 102.9, which were assigned to Si-C and Si-O bonds (Figure 3b) [53]. The existence of S 2p_{3/2} and 2p_{1/2} doublet for S 2p region at 163.8 and 164.9 was ascribed to C-S bonds (Figure 3c) [54]. XPS spectra in N 1s region showed two peaks located at 399.9 and 402.0, which corresponded to neutral and positively charged quaternary nitrogen (Figure 3d) [55,56]. Related peaks to Br 3d_{5/2} and Br 3d_{3/2} appeared at 67.5 and 67.9 confirming the presence of Br in the structure (Figure 3e) [57]. The Pd 3d spectrum could be deconvoluted into two doublets at 334.1 and 341.2 related to Pd(0) and 336.2 and 343.1 related to Pd(II) (Figure 3f) [58,59]. XPS result indicated that 57% of Pd was in its reduced form.

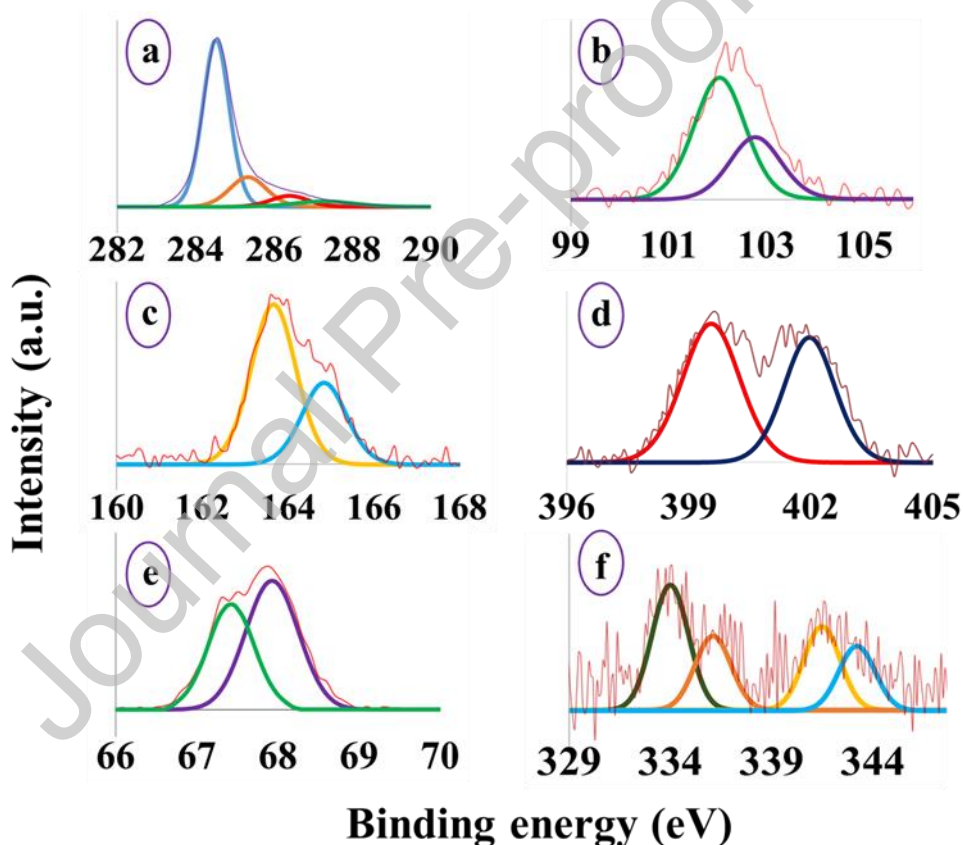


Figure 3: XPS spectrum of MWCNT@IL-Pd in a) C 1s, b) Si 2p, c) S 2p, d) N 1s, e) Br 3d and f) Pd 3d regions.

The thermal properties of MWCNT@IL3 were studied using thermogravimetric analysis (TGA). Results showed two main weight losses between 200-520 °C (Figure 4). The first one, around 200-500, was related to the decomposition of organic materials (including IL fragments) and second one, at 520

°C, is ascribed to the decomposition of CNT. It should be noted that MWCNT@IL3 decomposed at a significantly lower temperature than CNT-OH (hydroxylated CNT by using H₂O₂), due to the presence of Br⁻ anions and catalytic metal nanoparticles able to oxidize CNTs [60,61].

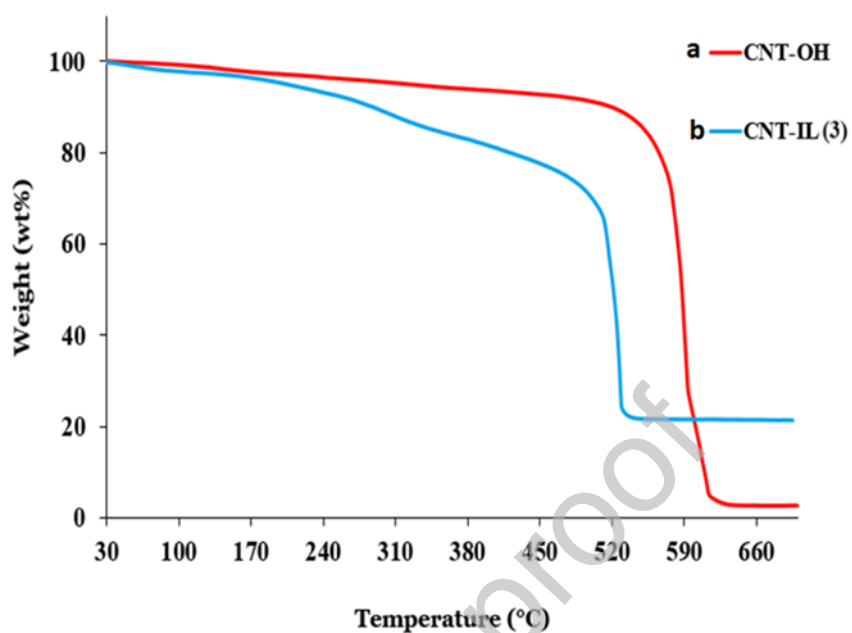


Figure 4: TGA diagram of a) CNT-OH; b) MWCNT@IL3

Scanning electron microscopy (SEM) images of MWCNT@IL-Pd showed an entangled structural morphology (Figure 5).

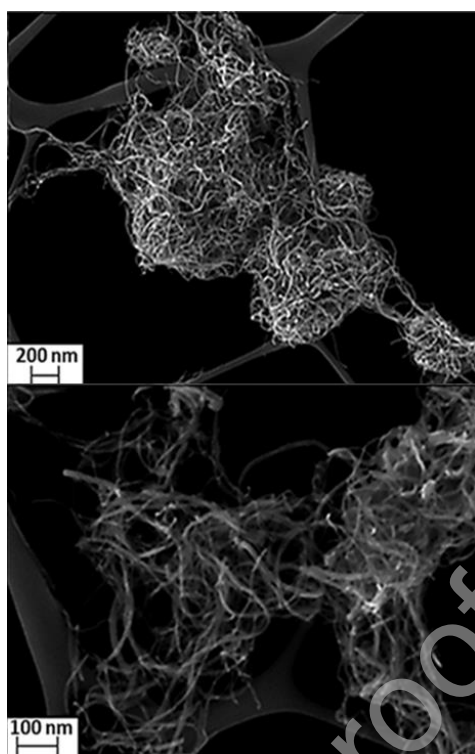


Figure 5: SEM images of MWCN@IL-Pd

Transmission electron microscopy (TEM) image of CNTs showed the presence of supported Pd nanoparticles in a range of 3-6 nm size (Figure 6).

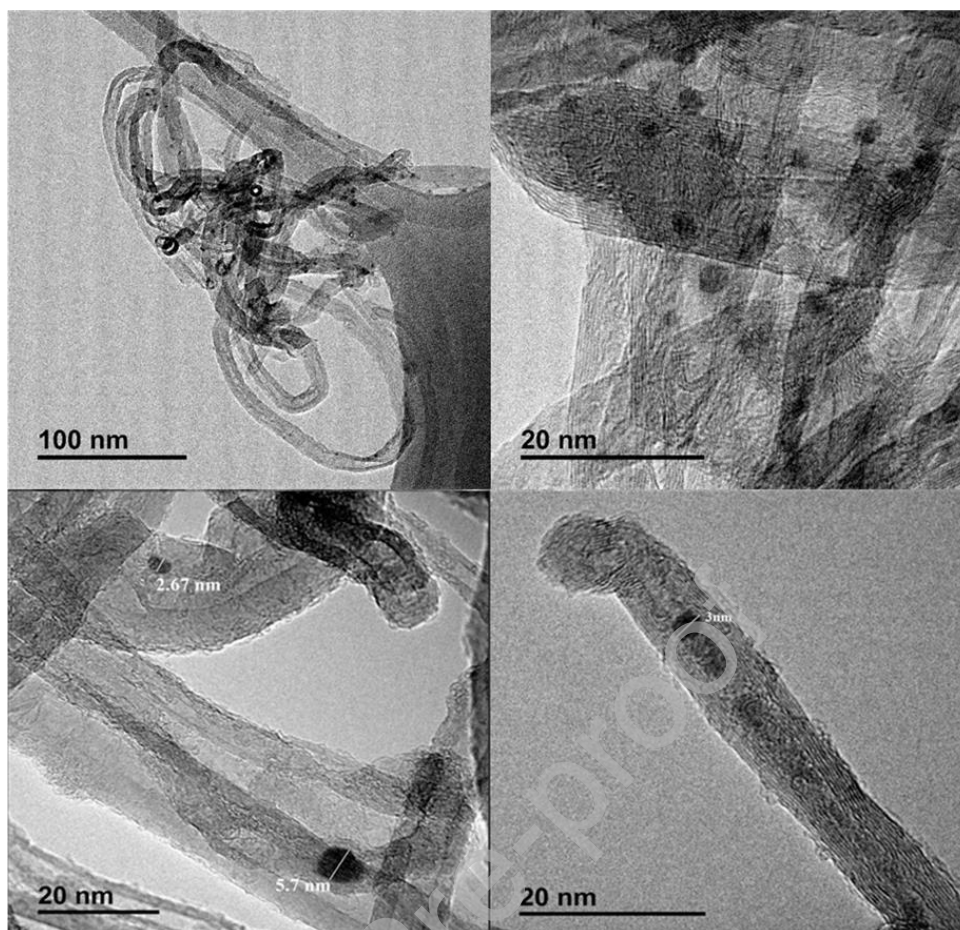
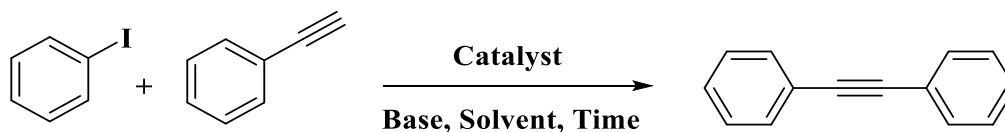


Figure 6: TEM images of MWCNT@IL-Pd

3.2. Catalytic performance

The prepared catalyst was assessed in the Sonogashira-Hagihara coupling reaction (Table 1). In order to find the optimized reaction conditions, the reaction of iodobenzene with phenylacetylene was selected and the effect of different factors such as solvent, base, catalyst loading and time was surveyed. Results showed that using 0.5 mol% of the catalyst excellent yields were obtained in DMF after 6 h, whilst lower yields were observed when the reaction was performed in toluene, Xylene, EtOH, and CH₃CN, H₂O and PEG-200 (Table 1, entries 1-9). Selecting DMF as a most efficient solvent, the effect of the base was next investigated (Table 1, entries 10-13). The best result corresponded to the reaction performed with DABCO rather than the other inorganic bases. Using DABCO as base, DMF as the solvent the lowering both of the reaction temperature and the catalyst amount, lower yields were obtained (Table 1, entries 14-16). Also, Sonogashira-Hagihara coupling reaction of iodobenzene and phenylacetylene was tested in the presence of MWCNT@IL-Pd catalyst without DABCO but any trace of the product was obtained (Table 1, entry 17).

Table 1. Optimization of the reaction conditions in the Sonogashira-Hagihara coupling reaction of iodobenzene with phenylacetylene.^a



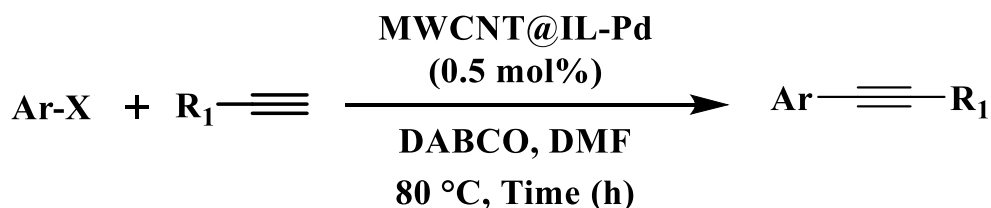
Entry	T (°C)	Base	Solvent	Catalyst (mol%)	Time (h)	Yield (%) ^b
1	80	DABCO	DMF	0.5	24	99
2	80	DABCO	DMF	0.5	12	96
3	80	DABCO	DMF	0.5	6	94
4	80	DABCO	Toluene	0.5	6	52
5	80	DABCO	Xylene	0.5	6	44
6	80	DABCO	CH ₃ CN	0.5	6	56
7	80	DABCO	PEG200	0.5	6	85
8	80	DABCO	EtOH	0.5	6	37
9	80	DABCO	H ₂ O	0.5	6	90
10	80	K ₂ CO ₃	DMF	0.5	6	17
11	80	Et ₃ N	DMF	0.5	6	58
12	80	Na ₂ CO ₃	DMF	0.5	6	31
13	80	NH ₄ OH	DMF	0.5	6	<5
14	60	DABCO	DMF	0.5	6	53
15	80	DABCO	DMF	0.3	6	80
16	80	DABCO	DMF	0.1	6	57
17	80	-	DMF	0.5	6	0



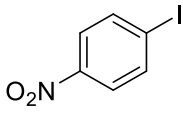
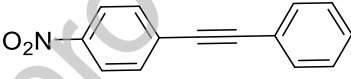
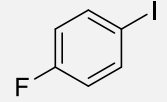
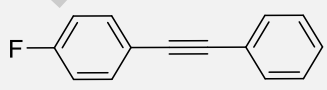
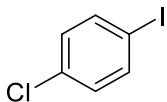
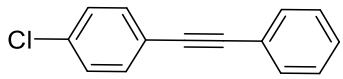
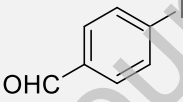
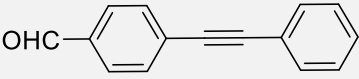
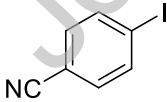
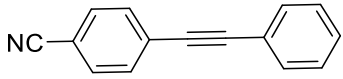
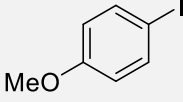
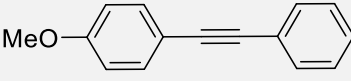
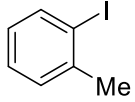
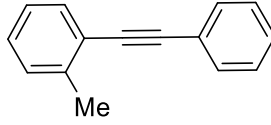
a) Reaction conditions: iodobenzene (0.5 mmol), phenylacetylene (0.75 mmol), base (0.75 mmol), Catalyst (see column) and solvent (2 mL).

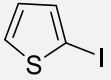
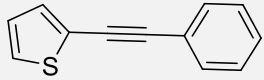
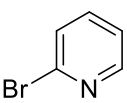
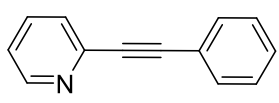
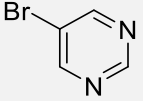
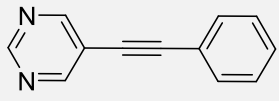
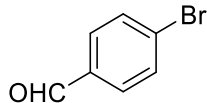
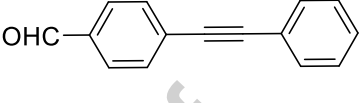
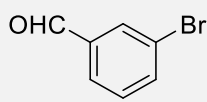
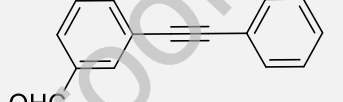
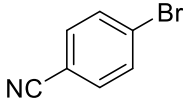
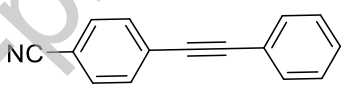
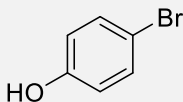
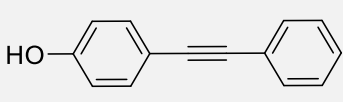
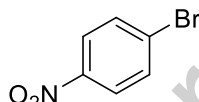
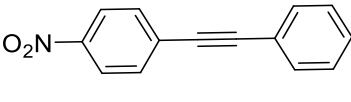
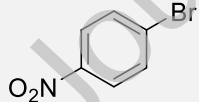
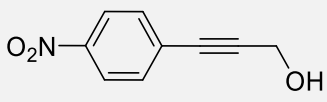
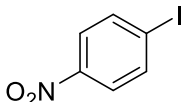
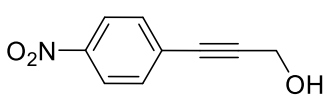
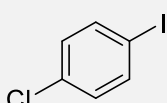
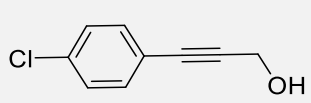
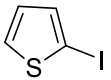
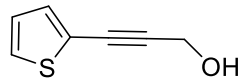
b) Yields were determined by GC.

Having optimized reaction conditions in hand, that means, DMF as solvent, DABCO as base, 0.5 mol% of catalyst at 80 °C, the coupling reaction between structurally different aryl halides and alkynes was studied (Table 2). Reactions of aryl iodides, having electron withdrawing groups such as $-\text{NO}_2$, $-\text{F}$, $-\text{Cl}$, $-\text{CHO}$, $-\text{CN}$, and aryl iodides having electron donating groups such as $-\text{Me}$ and $-\text{OMe}$ as well as iodobenzene, with phenylacetylene proceed satisfactorily and the desired aryl alkynes were obtained in 83-94% yields (Table 2, entries 1-8). Reaction of 2-iodothiophene with phenylacetylene was also performed in very high conversion affording the coupling product in 91% (Table 2, entry 9). Also, reactions of aryl bromides having both electron donating and withdrawing groups as well as challenging heterocyclic aryl bromides proceed efficiently and the corresponding products were isolated in excellent yields (Table 2, entries 10-16). It should be noted that reactions involving aryl iodides and bromides with propargyl alcohol were also accomplished and products were achieved in 81-86% yields (Table 2, entries 17-20). Since high yields were obtained in PEG200 and H_2O (Table 1, entries 7, 9), the Sonogashira-Hagihara reaction of some aryl halides in PEG200 and H_2O (Table 2, entries 2, 8-9, 14, 18) were performed. However, all the results indicated the formation of the desired products with lower yield than the obtained in the same reactions using DMF as solvent.

Table 2. Sonogashira-Hagihara coupling reaction of aryl and heteroaryl halides with terminal alkynes in the presence of the MWCNT@IL-Pd.^a



Entry	Ar-X	R ₁	Time (h)	Product	Yield (%) ^b	TOF ^g
1		C ₆ H ₅	6		94	31.3
2		C ₆ H ₅	8		90 ^d (80) ^c	22.5
3		C ₆ H ₅	12		89 ^d	14.8
4		C ₆ H ₅	12		90	15
5		C ₆ H ₅	10		91 ^d	18.2
6		C ₆ H ₅	10		90	18
7		C ₆ H ₅	20		93	9.3
8		C ₆ H ₅	17		83 ^d (70) ^c	9.7

9		C ₆ H ₅	6		91 ^d (81) ^c	30.3
10		C ₆ H ₅	6		78 ^{d,e}	26
11		C ₆ H ₅	10		82 ^{d,e}	16.4
12		C ₆ H ₅	8		94 ^e	23.5
13		C ₆ H ₅	10		84 ^e	16.8
14		C ₆ H ₅	8		89 ^e (60) ^f (45) ^c	22.2
15		C ₆ H ₅	15		86 ^e	11.4
16		C ₆ H ₅	6		97 ^e	32.3
17		-CH ₂ OH	6		81 ^{d,e}	27
18		-CH ₂ OH	8		83 ^d (70) ^f	20.7
19		-CH ₂ OH	12		84 ^d	14
20		-CH ₂ OH	6		86 ^d	28.6

a) Reaction conditions: aryl halide (0.5 mmol), terminal alkyne (0.75 mmol), DABCO (0.75 mmol), catalyst (25 mg) and DMF (2 mL).

b) Yields were determined by GC.

c) Reaction condition: aryl halide (0.5 mmol), terminal alkyne (0.75 mmol), DABCO (0.75 mmol), Catalyst (25 mg) and PEG200 (2 mL).

d) Isolated yields after purification.

e) The reaction was performed at 100 °C.

f) Reaction condition: aryl halide (0.5 mmol), terminal alkyne (0.75 mmol), DABCO (0.75 mmol), Catalyst (25 mg) and H₂O (2 mL).

g) [TOF] values [(mol product/mol catalyst)/time of reaction (h)].

3.3. Recycling of the catalyst

Since one of the most important advantages of heterogeneous catalysts is their recovering and recycling, recycling of MWCNT@IL-Pd after this Sonogashira-Hagihara coupling reaction of iodobenzene with phenylacetylene and 4-bromonitrobenzene with phenylacetylene under the optimized reaction conditions were studied. Results showed that this catalyst was successfully recovered and reused for five consecutive runs with small decrease in activity (Figure 7).

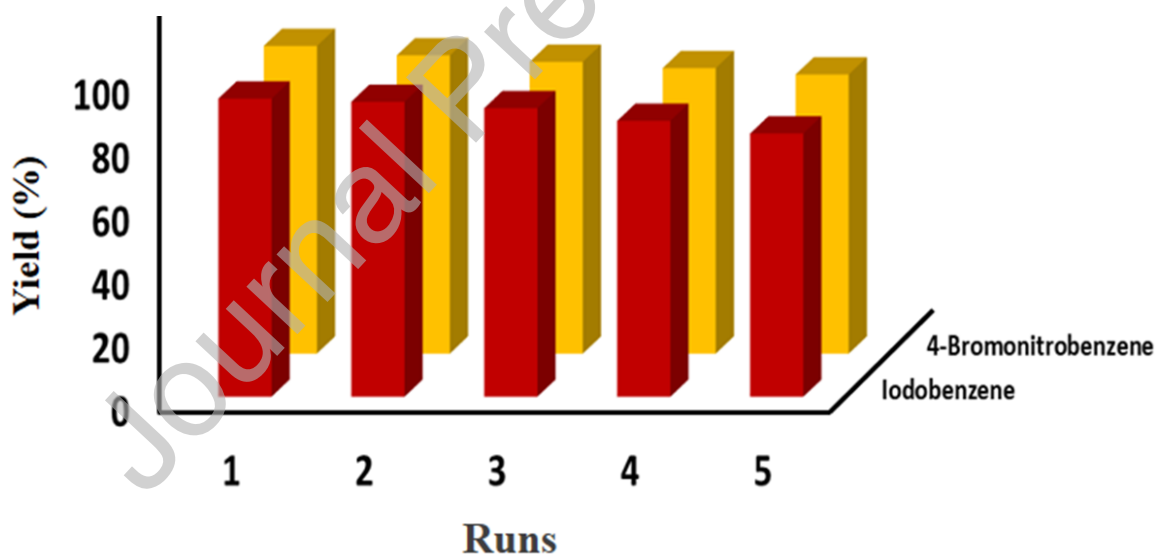


Figure 7: Recycling of the catalyst for the reaction of iodobenzene with phenylacetylene (red) and 4-bromonitrobenzene with phenylacetylene (yellow)

EDX spectrum of the reused catalyst after the 3rd consecutive run showed the presence of elements analogously to the observed ones in the fresh catalyst spectrum (Figure 8).

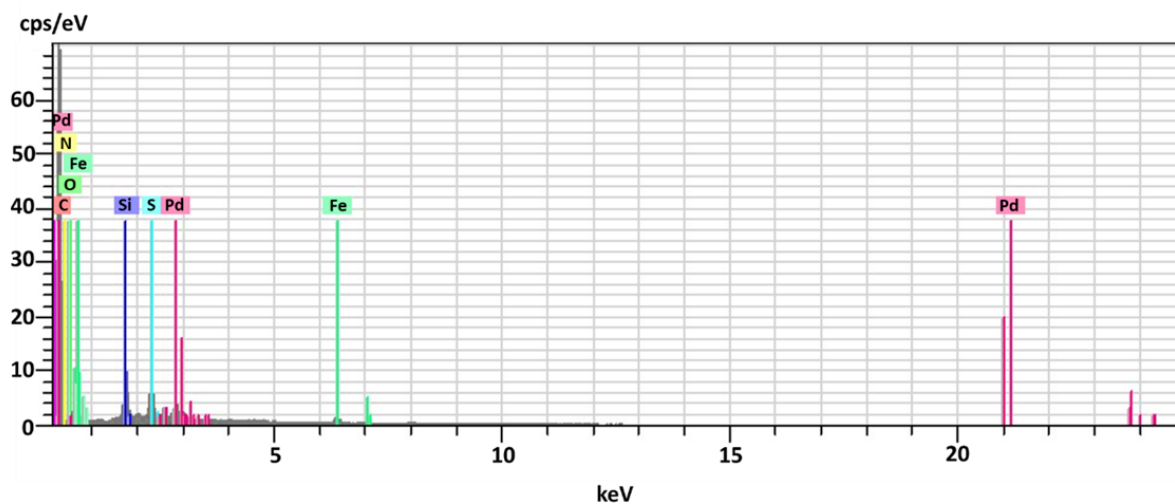


Figure 8: EDX expectrum of reused catalyst after 3rd run.

Also, SEM and TEM (Figures 9 and 10) images of the reused catalyst after 3rd run were analyzed and the results showed similar pattern to the obtained ones for the fresh catalyst, indicating the preservation of the catalyst structure with small aggregation of Pd NPs.

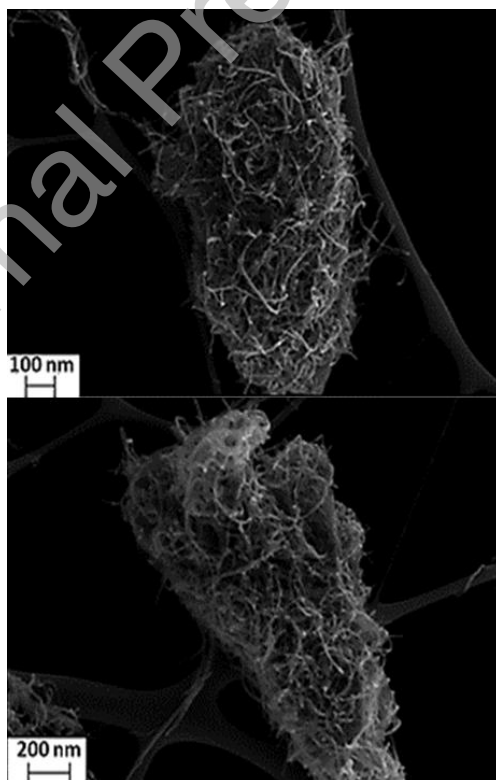


Figure 9: SEM images of reused catalyst after the 3rd run.

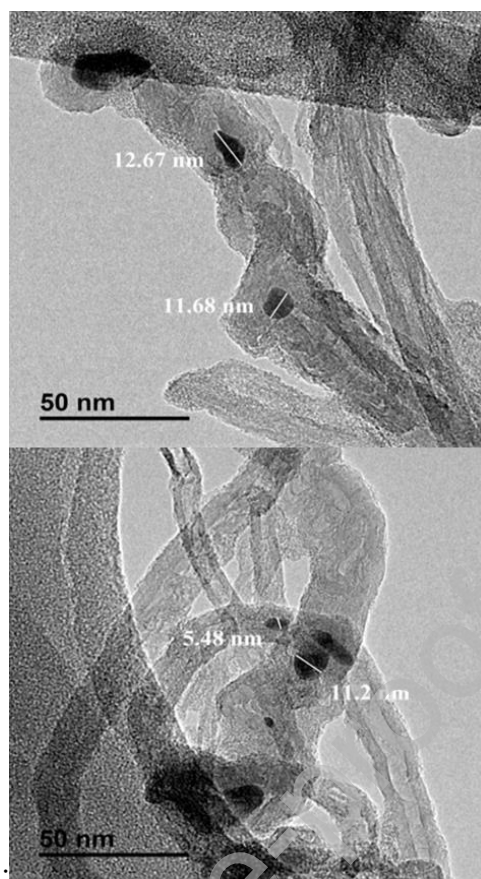


Figure 10: TEM images of reused catalyst after the 3rd run.

Finally, in order to find some information about homogeneous or heterogeneous nature of the catalyst, two important tests, including hot filtration and poly(4-vinyl-pyridine) (PVPy) addition, were investigated (Figure 11)[62]. In the case of hot filtration, the reaction mixture (iodobenzene and phenylacetylene) was filtered after 2 h. At this moment, the conversion of the reaction was 40% according to GC plot. The resulting solution obtained by hot filtration was allowed to proceed under optimized conditions during 6 additional hours. GC analysis of the reaction showed a 51% conversion for diphenylacetylene (Figure 11). In the next experiment PVPy (in molar ratio to [Pd]~400) was added at the beginning of the reaction between iodobenzene and phenylacetylene under optimized reaction conditions. It is worth mentioning that PVPy is strong poisoning polymer for homogeneous catalysts. Results of PVPy test indicated that the reaction proceeded similarly to standard reaction affording slightly less yield than normal reaction conditions (Figure 11). It is proved that heterogeneous catalysts lose their activity in the presence of mercury, although recent studies revealed that this experiment must be carefully observed. When we added 150 equiv. of mercury per equivalent of palladium at the beginning of the reaction of iodobenzene with phenylacetylene under optimized conditions, the reaction did not proceed satisfactorily obtaining a 10% of product only. According to all these three results, we could conclude that this catalyst mainly operated under heterogeneous conditions with negligible leaching of the Pd loading [63-65].

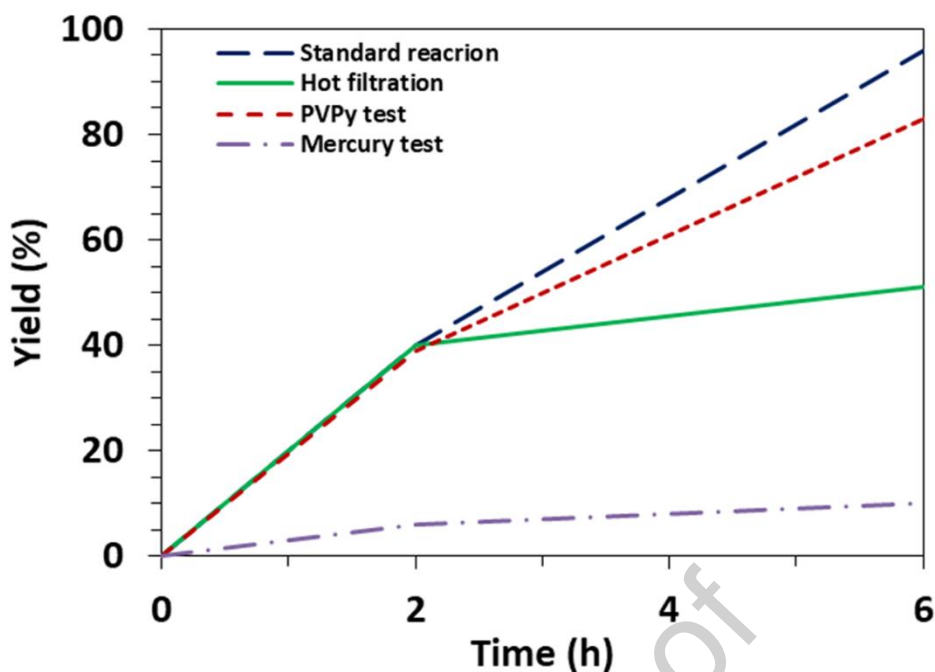
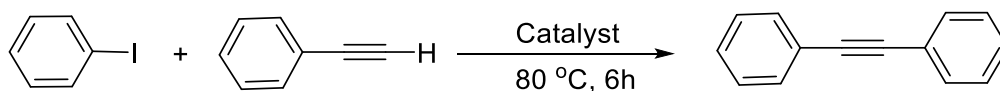


Figure 11: PVP poisoning, mercury poisoning and hot filtration tests for the MWCNT@IL-Pd catalyzed Sonogashira-Hagihara reaction of iodobenzene and phenylacetylene.

In order to show the important role of IL in structure, the catalytic activity of MWCNT@IL-Pd was compared with other prepared intermediate catalysts shown in Scheme 2 such as CNT, Pd/CNT and Pd/CNT-OH as well as the commercially available Pd/C (Table 3, entries 1-3). As it is depicted in Table 3, results showed that MWCNT@IL-Pd had the highest activity. Also, the recycling of the Pd/CNT-OH was investigated for 4 runs in the bench reaction but rapidly failed after 1th possibly due to the leaching of Pd during reaction in the absence of IL (Table 3, entries 4-7). Furthermore, we also prepared other catalyst *via* reaction of thiol functionalized MWCNTs with 1-benzyl-3-vinyl-1H-imidazole-3-ium and resulting material was used for stabilization of Pd (depicted as a MWCNT@ILBVI-Pd in Table 3). Using this catalyst, with same Pd amount in the reaction of iodobenzene with phenylacetylene under optimized reaction condition 76% yield was obtained. Recycling of this catalyst demonstrated that yield was decreased to 45% in second run and to 35 in 3rd run (Table 3, entries 8-10).

Table 3. Comparative catalytic activity of MWCNT@IL-Pd with other catalysts in Sonogashira coupling reaction of iodobenzene with phenylacetylene.

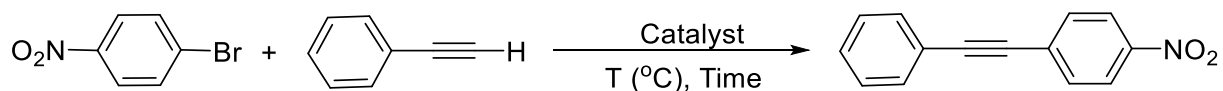


Entry	Catalyst	Condition	Yield (%)
1	CNT	DMF, DABCO	2
2	Pd/CNT	DMF, DABCO	35
3	Pd/C	DMF, DABCO	10
4	Pd/CNT-OH (Run 1)	DMF, DABCO	90
5	Pd/CNT-OH (Run 2)	DMF, DABCO	50
6	Pd/CNT-OH (Run 3)	DMF, DABCO	10
7	Pd/CNT-OH (Run 4)	DMF, DABCO	2
8	MWCNT@ILBVI-Pd (Run 1)	DMF, DABCO	76
9	MWCNT@ILBVI-Pd (Run 2)	DMF, DABCO	45
10	MWCNT@ILBVI-Pd (Run 3)	DMF, DABCO	35

^a Reaction condition: aryl halide (0.5 mmol), terminal alkyne (0.75 mmol), DABCO (0.75 mmol), DMF (2 mL) and catalyst (0.5 mol% Pd).

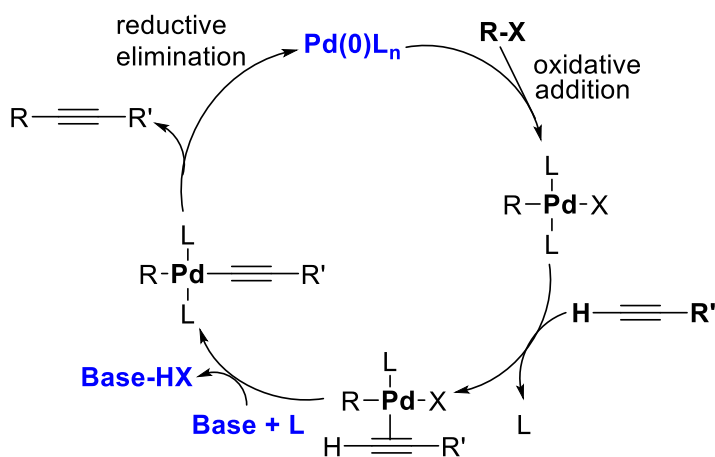
We have also compared catalytic activity of MWCNT@IL-Pd with some other catalysts in Sonogashira-Hagihara reaction of 4-bromonitrobenzene and phenylacetylene as a common reaction. In Table 4, the overall high catalytic activity and robustness of the titled catalyst is demonstrated.

Table 4. Comparative catalytic activity of MWCN@IL-Pd with other reported catalysts in Sonogashira coupling reaction of 4-bromonitrobenzene and phenylacetylene.



Entry	Catalyst	T (°C), time (h)	Pd loading	Yield (%)	TOF	Refs.
1	Pd/MIL-101	6 h, 130 °C	3.5% wt	90	4.6	[66]
2	CPS-MNPs-NNN-Pd	24 h, 90 °C	0.5 mol%	80	6.6	[67]
3	Pd/PEG-functionalized silica	7 h, 110 °C	1 mol%	94	13.4	[68]
4	Pd@Fe ₃ O ₄	24 h, 110 °C	1 mol%	68	2.8	[69]
5	G3-Gu-Pd	12 h, 100 °C	1 mol%	90	7.5	[70]
6	SBA-15-EDTA-Pd	6 h, 120 °C	2.5% wt	99	8.2	[71]
7	PdTSPc@KP-GO	9 h, 100 °C	1 mol%	95	10.5	[72]
8	PdNPs@NCmw	24 h, 90 °C	10% wt	85	0.38	[73]
9	MWCN@IL-Pd	6 h, 100 °C	0.5 mol%	97	32.3	This work

The proposed mechanism for this copper-free MWCNT@IL-Pd catalyzed Sonogashira-Hagihara reaction involves a well-known cycle including oxidative addition of aryl halide to Pd(0), complexation and addition of alkyne to Pd and reductive elimination step which produce desired product and regenerate Pd(0) [10-11].



Scheme 3: Proposed C–C coupling reaction mechanism by using MWCNT@IL-Pd catalyst.

4. Conclusion

In summary, a new ionic liquid modified carbon nanotube supported Pd NPS, MWCNT@IL-Pd, was developed. This new catalyst has shown high catalytic activity in the Sonogashira-Hagihara reaction of aryl iodides and bromides. This catalyst can be easily recoverable by centrifugation and recycled for five runs with small decrease of activity. The heterogeneous nature of the catalysts was confirmed after hot filtration and addition of PVPy and Mercury. Catalyst robustness is excellent allowing to reuse the same catalyst up to more than 5 consecutive batches ensuring very high yields (up to 97%).

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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