

Catalytic Evaluation of Palladium Nanoparticles on Silica-Grafted *n*-Propyl-Diaza-15-Crown-5 (PNP-SGPDC) in the Heck and Suzuki Reactions

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Silica-grafted *n*-propyl-diaza-15-crown-5 (SGPDC) with immobilized palladium nanoparticles was found as an efficient heterogeneous catalytic system for the Heck and Suzuki coupling reactions and satisfied results were obtained. Different derivatives of aryl halides and alkenes under the Heck reaction were converted to the corresponding products with good efficiency. The presence of electron-donating groups on the aryl moiety of aryl halide derivatives retarded the reaction and led to the drop of yields. In contrast, higher efficiency was observed when electron-withdrawing groups were accommodated on the aryl halide. As well as, a variety of bi-phenyl derivatives were well synthesized by the coupling reaction between aryl halides and aryl boronic acids derivatives *via* the Suzuki reaction. Reusability of the catalyst was examined in both Heck and Suzuki reactions under optimized conditions. The catalyst could be recycled several times without any treatment in its catalytic activity. The TEM image of the catalyst utilized in the Heck reaction after seven times of recyclability indicates that the morphology and size of the nanoparticles have remained almost intact.

Keywords: Aza-crown ether, Heterogeneous catalysis, Palladium nanoparticle, Heck reaction, Suzuki reaction

INTRODUCTION

Cross coupling reactions, especially C-C couplings have aroused considerable interests in the past decades. Among various coupling reactions comprising Heck [1-2], Suzuki [3], Sonogashira [4], Stille [5], Negishi [6], Kumada [7] and Hiyama [8] reactions, the Heck reaction and the Suzuki-Miyaura coupling reaction have taken up a specific position in organic chemistry for which they have found fundamental applications in every area of organic synthesis [9-10]. Since their discovery, considerable attempts have been devoted to conducting these reactions under milder and environmentally benign conditions. Low reaction temperature, non-toxic solvents, inexpensive reagents and catalyst recycling have been always of primary importance hence much time has been allocated to improve these conditions. Reusability of the catalyst is especially desired on account of satisfying economic and environmental

concerns. This becomes substantially critical when an expensive and toxic transition metal is utilized as the catalyst. However, major efforts in this direction have been concentrated to design the heterogeneous catalytic systems based on inexpensive and environmentally friendly materials. Although, the homogenous catalysts offer great advantages such as acceleration in the reaction rate, high turnover number (TON), excellent selectivity and favorable yields, they have problems in being recycled leading to a loss of expensive metal and ligands [11-14].

As mentioned before, recycling of the catalyst is in demand to preclude catalyst loss. In this respect, endeavors gave rise to immobilization of palladium-as catalyst in coupling reactions especially Heck and Suzuki- on various solid supports such as metal oxides (Pd-MgO, Pd-TiO₂, Pd-Al₂O₃, Pd-Fe₃O₄) [15-16], organic polymers [17-18], layered clays [19-20], activated carbon [21] and tripodal phosphine ligands [22]. However, among all these, silica seems to be superior owing to its wide accessibility, excellent stability and porous nature. The other virtue of this

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solid support is that most of the organic functional groups can be bound to the surface of silica resulting in facile coupling [23]. It is worth mentioning that Pd can be either directly deposited onto silica, or it can be anchored as a complex. In the former, deposit is formed by the virtue of high surface area of silica giving rise to better catalytic activity for Pd. In this context, agglomeration and leaching of nanoparticles are two serious problems that may be posed while using this kind of catalyst. One solution to preclude these shortcomings is to accommodate suitable ligands on silica. Developing new approaches, many examples of silica-supported palladium have been given out in recent years by various research groups, being used in coupling reactions especially Heck and Suzuki couplings [24-25]. Although good progress has been made and miscellaneous conditions have been offered, efforts in this area are being continued and needs still remain to find heterogeneous and environmentally friendly catalytic systems.

Having this end in view, a number of ligands have been postulated to gratify these criteria. Among them, oxygen-content macrocycles such as crown ethers are well known to have strong tendency to complex alkali and alkaline earth ions [26]. In contrast, polyazamacrocycles show a high affinity for transition metal ions. Aza-crown ethers are found to possess features in between and form complexes with both kinds of ions [27-29]. These mixed complexation properties render aza-crowns appealing to researchers and this is why they have found use as catalyst in nucleophilic substitution and oxidation reactions [30-31], in the design of chromogenic reagents that are sensitive to alkali and alkaline earth metal cations, and liquid-liquid extraction of alkali and alkaline earth metal cations [32-33]. Exploiting this unique feature of macrocycles with some heteroatoms in their structure, in 2008, Sun *et al.* introduced a new catalytic system based on Pd and aza-crown ethers [34]. This system benefited from both flexible macrocyclic scaffold and chelating effect of *N*- or *O*-containing ligands assisted in stabilizing along with activating the catalytic species. Despite achieving good results in Suzuki reaction, the ligand and catalyst recovery remained a challenge. Hence, we are going to introduce a new catalytic system based on palladium nanoparticles deposited on silica which is modified by diaza-crown ether as a stabilizer of nanoparticles. Recently, we have managed to link diaza-15-

crown-5 to the silica-surface by the aid of propyl amine as a linker and subsequently immobilized with palladium nanoparticles for solid phase extraction and preconcentration of some metal ions [35]. In this paper and in pursuit of our interests in the design and preparation of heterogeneous catalytic systems based on silica and application of them in coupling reactions [36-39], the Heck and Suzuki cross-couplings were tested in the presence of this catalytic system which not only resulted in good results but the sustainability of palladium nanoparticles deposited on silica substrate was also noticeable.

EXPERIMENTAL

Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. The products were characterized by comparison of their spectral and physical data with those reported in literature. For recorded ¹H NMR spectra we used Bruker Avance (300 MHz or DRX 500 MHz) or Bruker Ultrashield (400 MHz) and pure deuterated CDCl₃ as solvent with tetramethylsilane (TMS) as internal standard. X-ray diffraction (XRD, D8, Advance, Bruker, axs), (TEM (Hitachi H-800 TEM at an operating voltage of 200 Kv), FT-IR spectroscopy (Shimadzu FT-IR 8000 spectrophotometer), and SEM instrumentation (SEM, XL-30 FEG SEM, Philips, at 20 kV) were employed for characterization of the catalyst. Surface spectroscopic analysis of the catalyst was performed in an ESCA/AES system. This system is equipped with a concentric hemispherical (CHA) electron energy analyzer (Specs model EA10 plus) suitable for X-ray photoelectron spectroscopy (XPS). Melting points were determined in open capillary tubes in a Barnstead Electrothermal 9100 BZ circulating oil melting point apparatus. The reaction monitoring was accomplished by TLC on silica gel PolyGram SILG/UV254 plates. Column chromatography was carried out on columns of silica gel 60 (70-230 mesh). All the products were characterized with IR and NMR and the known compounds were compared with those reported in literature.

Preparation of Catalyst

Preparation of Silica-grafted 3-chloropropyl (3-CPS).

The activated silica (25.0 g) was suspended in 300 ml of dry

toluene and then an excess of 3-chloropropyl-trimethoxysilane (25.0 ml) was added, followed by addition of 2.5 ml of triethylamine (as the base) [36]. The suspension was magnetically stirred and refluxed for 48 h. The reaction was then stopped and the resultant modified silica cooled to room temperature, transferred to a vacuum glass filter, and washed first with a mixture of toluene and ethanol-water, then with deionized water and eventually with methanol. Chloropropyl silica was dried under vacuum at 60 °C for 4 h. Elemental analysis showed 9.16% C and 1.76% H (~1.90 mmol g⁻¹).

Synthesis of silica-grafted *n*-propyl-diaza-15-crown-5. To a magnetically stirred mixture of 3-chloropropylsilica (10 g) in dry CHCl₃ (50 ml), diaza-15-crown-5 (25 mmol), and some drops of triethyl amine were added and refluxed for 24 h. Next, the mixture was filtered and washed with dichloromethane (3 × 10 ml) and ethanol (3 × 10 ml). Having been dried in oven (at 70 °C for 4 h), silica-grafted *n*-propyl-diaza-15-crown-5 (SGPDC) was obtained as a white powder. Elemental analysis was as follows: 31.08% C, 5.55% H and 5.21% N (~1.85 mmol g⁻¹).

Immobilization of Pd nanoparticles on silica-grafted *n*-propyl-diaza-15-crown-5. To a mixture of SGPDC (1 g) in absolute ethanol (10 ml), palladium acetate (168 mg, 0.75 mmol) was added and stirred for 24 h at room temperature. Then, the mixture was filtered, washed with ethanol (3 × 10 ml) and vacuum dried (at 70 °C for 4 h). Immobilized Pd nanoparticles on SGPDC was obtained as a dark solid (0.73 mmol Pd/g assigned by EDX and ICP).

General procedure for the Heck cross-coupling reaction. To a mixture of aryl halide (1 mmol), alkene (1.2 mmol), and Na₂CO₃ (2.5 mmol) in 3 ml DMF, catalyst (0.03 g, 2.2 mol%) was added and heated on oil bath at 120 °C. The reaction was continuously followed by TLC to completion. Successively, the mixture was cooled down to room temperature and filtered, and then the residue was washed with dichloromethane (2 × 10 ml) in order to purify the catalyst. Having extracted the reaction mixture from dichloromethane and water, the organic phase was dried over Na₂SO₄. Evaporation of the solvent gave products. For further purification, the products passed through a short column of silica gel using *n*-hexane as eluent.

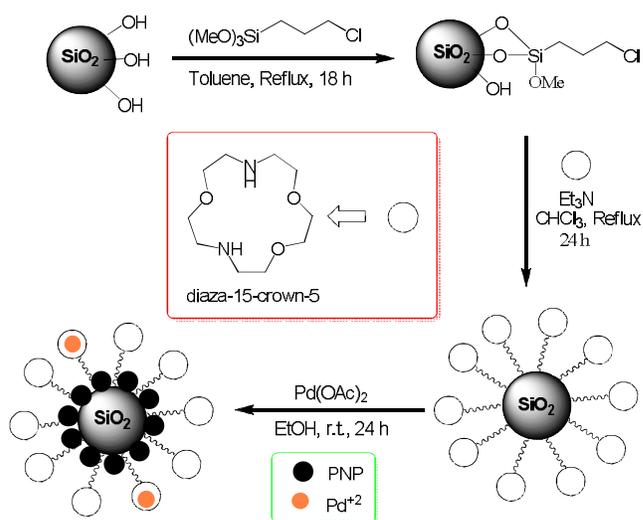
General procedure for the Suzuki cross-coupling reaction. To a mixture of aryl halide (1 mmol), aryl boronic

acid (1.2 mmol), and Na₂CO₃ (2.5 mmol) in 2 ml water, catalyst (0.03 g, 2.2 mol%) was added and heated on oil bath at 80 °C and the reaction was followed by TLC. After completion of the reaction, the mixture was cooled down to room temperature and filtered, and the remaining was washed with dichloromethane (3 × 10 ml) in order to purify the catalyst. After extraction dichloromethane from water, the organic phase was dried over Na₂SO₄. Evaporation of the solvent gave products. For further purification, the products passed through a short column of silica gel using *n*-hexane as eluent.

RESULTS AND DISCUSSIONS

The synthetic route for the preparation of palladium nanoparticles on silica-grafted *n*-propyl-diaza-15-crown-5 (PNP-SGPDC) is shown in Scheme 1. The reaction of activated silica with 3-chloropropyl trimethoxysilane in refluxing toluene resulted in the production of silica-grafted *n*-propyl chloride. Subsequently, diaza-15-crown-5 was reacted with this modified silica to generate the SGPDC. Finally, palladium acetate was reduced on the modified silica surface using EtOH as a reducing agent [40-41].

The structure of the catalyst was characterized by some spectroscopic and microscopic techniques such as Infrared



Scheme 1. The synthetic route for the preparation of PNP-SGPDC

spectroscopy (FT-IR), X-ray diffraction spectroscopy (XRD), Inductively coupled plasma (ICP), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). (See Supporting Information). According to the TEM micrograph, the average size of the palladium nanoparticles supported on silica was obtained 12 nm (Fig. 1).

Catalytic activity of PNP-SGPDC was scrutinized in the Heck and Suzuki cross-coupling reactions. Therefore, we screened various conditions to determine the optimization conditions in the Heck reaction between bromobenzene and ethyl acrylate (Table 1). This reaction was not accomplished in the absence of catalyst even after 24 h at 120 °C (Table 1, entry 1). The optimized amount of catalyst was 0.03 g (2.2 mol% of Pd). By decreasing the amount of the catalyst to 0.01g (0.73 mol% of Pd), the yield of product dropped contrary to the time of reaction which increased (Table 1, entry 3). In contrast, when the catalyst loading increased to 0.05 g (3.6 mol% of Pd) no marked difference was observed in the reaction yield (Table 1, entry 4). Moreover, other parameters such as solvent, base and temperature were also examined and the results were depicted in Table 1. As can be seen in this Table, under the following conditions the best yields were obtained: aryl halide (1 mmol), ethyl acrylate (1.2 mmol), Na₂CO₃ (2.5 mmol), and catalyst (0.03 g, 2.2 mol% of Pd) in 3 ml DMF at 120 °C.

This protocol was also extended to other alkenes which demonstrated satisfactory results irrespective of the alkene which was used (Table 2). As expected, the presence of electron-donating groups on the aryl moiety of aryl halide derivatives retarded the reaction and led to the drop of yields (Table 2, entries 3, 4, 7 and 8). In contrast, higher efficiency was observed when electron-withdrawing groups were accommodated on the aryl halide (Table 2, entries 9-11). Iodobenzene was also used to react with styrene and ethyl acrylate which afforded a short reaction time and high isolated yields (Table 2, entries 12 and 13).

The scope of this catalyst was further explored. To meet this target, it was used in the Suzuki reaction and the reaction of bromobenzene and phenylboronic acid was studied as a model reaction in the presence of the foregoing catalyst. After checking the different parameters such as solvent, temperature, and catalyst loading (Table 3), the

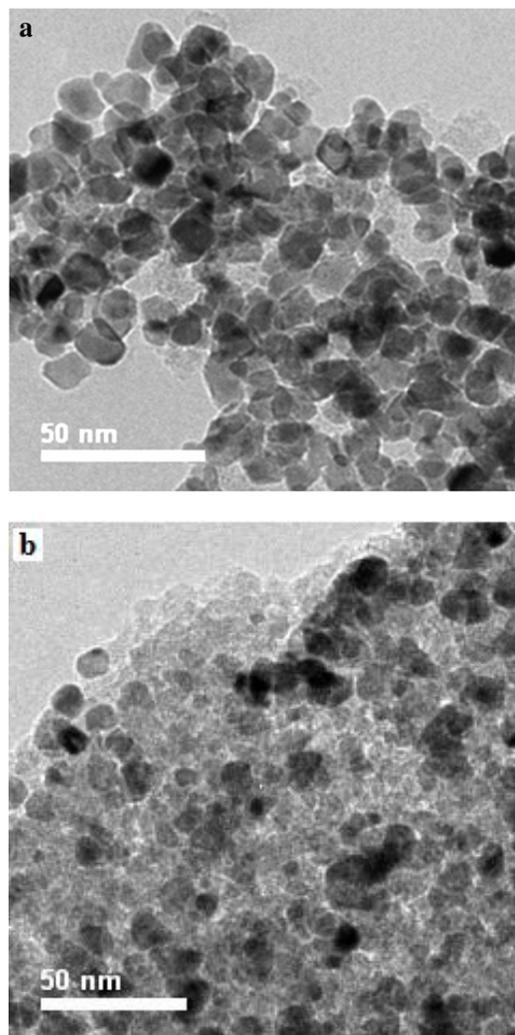
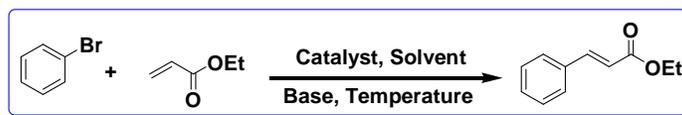


Fig. 1. TEM micrograph of catalyst (a) before and (b) after seven reusability in the Heck reaction

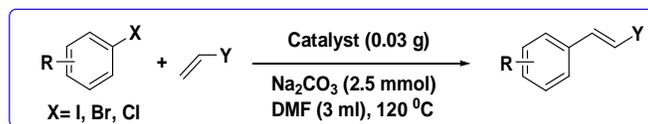
following conditions were found to give the optimum yield: aryl halide (1 mmol), aryl boronic acid (1.2 mmol), Na₂CO₃ (2.5 mmol), catalyst (0.03 g, 2.2 mol% of Pd) in 3 ml of water at 80 °C.

The generality of this reaction was evaluated for other aryl halides having different steric and electronic properties. The results are summarized in Table 4. Phenylboronic acid was found to be smoothly coupled with bromobenzene providing an excellent yield (87%) of the desired product. The reaction also worked well with less reactive

Table 1. Optimization of the Heck Reaction Conditions Between Bromobenzene and Ethyl Acrylate under Various Conditions^a

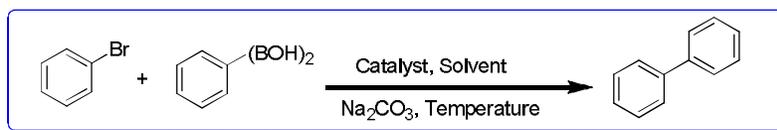
Entry	Solvent	Base	Catalyst (g)	Temp. (°C)	Time (h)	Yield (%) ^b
1	DMF	Na ₂ CO ₃	0.0	120	24	0
2	DMF	Na₂CO₃	0.03	120	12	89
3	DMF	Na ₂ CO ₃	0.01	120	48	78
4	DMF	Na ₂ CO ₃	0.05	120	12	89
5	DMF	K ₂ CO ₃	0.03	120	48	71
6	DMF	Cs ₂ CO ₃	0.03	120	48	68
7	DMF	Et ₃ N	0.03	120	48	56
8	Toluene	Na ₂ CO ₃	0.03	Reflux	48	50
9	THF	Na ₂ CO ₃	0.03	Reflux	48	48
10	H ₂ O	Na ₂ CO ₃	0.03	Reflux	48	51
11	CH ₃ CN	Na ₂ CO ₃	0.03	Reflux	48	47
12	DMF	Na ₂ CO ₃	0.03	140	12	79
13	DMF	Na ₂ CO ₃	0.03	80	48	57

^aReaction conditions: bromobenzene (1 mmol), ethyl acrylate (1.2 mmol) and base (2.5 mmol) in solvent (3 ml). ^bIsolated yield.

Table 2. The Heck Reaction Catalyzed by PNP-SGPDC^a

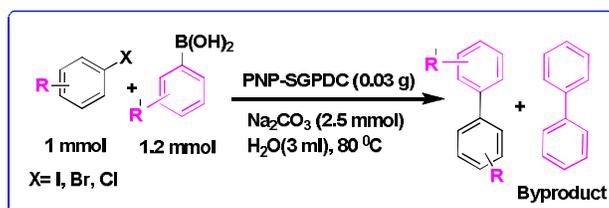
Entry	X	R	Y	Time (h)	Yield (%) ^b
1	Br	H	COOEt	12	89
2	Cl	H	COOEt	48	68
3	Br	OMe	COOEt	12	80
4	Cl	OMe	COOEt	48	67
5	Br	H	Ph	6	88
6	Cl	H	Ph	24	73
7	Cl	OMe	Ph	24	68
8	Cl	Me	Ph	24	70
9	Cl	CN	Ph	12	90
10	Cl	NO ₂	Ph	12	92
11	Br	NO ₂	Ph	6	95
12	I	H	Ph	1	95
13	I	H	COOEt	1	94

^aReaction conditions: aryl halide (1 mmol), alkene (1.2 mmol), Na₂CO₃ (2.5 mmol), catalyst (0.03 g), DMF (3 ml) at 120 °C. ^bIsolated yield.

Table 3. Optimization of the Suzuki Reaction Conditions Between Bromobenzene and Phenylboronic Acid under Various Conditions^a

Entry	Solvent	Catalyst (g)	Temp. (°C)	Time (min)	Yield (%) ^b
1	H ₂ O	0.01	80	240	70
2	H₂O	0.03	80	60	87
3	H ₂ O	0.05	80	60	89
4	H ₂ O	0.075	80	60	89
5	DMF	0.03	80	160	75
6	Toluene	0.03	Reflux	120	50
7	THF	0.03	Reflux	120	45
8	CH ₃ CN	0.03	Reflux	180	65
9	C ₂ H ₅ OH	0.03	Reflux	240	80

^aReaction conditions: bromobenzene (1 mmol), phenylboronic acid (1.2 mmol) and Na₂CO₃ (2.5 mmol) in solvent (3 ml). ^bIsolated yield.

Table 4. The Suzuki Reaction Catalyzed by PNP-SGPDC^a

Entry	X	R	R'	Time (h)	Yield (%) ^b	by product (%) ^c
1	Br	H	H	1	87	-
2	Cl	H	H	5	65	-
3	Br	4-OMe	H	5	83	13
4	Cl	4-OMe	H	8	62	18
5	Br	4-Me	H	5	81	10
6	Cl	4-Me	H	10	60	15
7	Br	4-SMe	H	5	81	8
8	Cl	4-OMe	4-Et-	12	71	10
9	Br	4-OMe	4-Et-	5	83	7
10	Cl	4-NO ₂	H	3	73	12
11	Br	4-NO ₂	H	0.5	73	12
12	Br	2-Me-4-NO ₂	H	3	75	10
13	Cl	2-Me	4-Et-	12	73	11
14	Br	Br	4-Et-	8	70	8 ^d
15	I	H	H	0.5	97	-

^aReaction conditions: aryl halide (1 mmol), boronic acid (1.2 mmol), Na₂CO₃ (2.5 mmol), catalyst (0.03 g), water (3 ml) at 80 °C. ^bIsolated yield. ^cGC yield. ^d2.4 mmol of boronic acid and 0.06 g of catalyst was used.

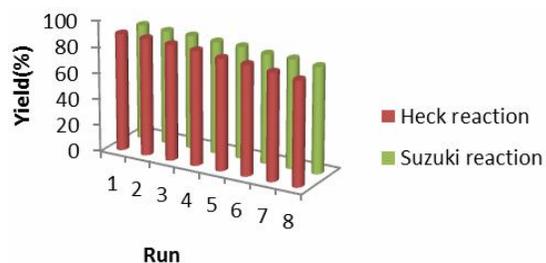


Fig. 2. Reusability of PNP-SGPDC catalyst in the Heck and Suzuki reactions

chlorobenzene giving 65% of the yield. Electron withdrawing groups such as nitro (Table 4, entries 10, 11 and 12), and donating groups such as methyl, methoxy, and methylthio (Table 4, entries 3-9), were well tolerated under this catalytic system. Sterically hindered 2-methylchlorobenzene was coupled with ethyl benzene boronic acid providing 73% of the desired product (Table 4, entry 13). In the case of 1,4-dibromo benzene, both bromine groups were replaced by phenyl group after 8 h of reaction time (Table 4, entry 14). When iodobenzene was reacted with phenyl boronic acid, high yield in a short reaction time was obtained (Table 4, entry 15). It is noteworthy that biphenyl is obtained as a trivial by-product in the Suzuki reaction. Amount of this by-product for different reagents is shown in Table 4.

Recycling of the catalyst in both Heck and Suzuki reactions under optimized conditions were examined. To this end, after completion, reaction mixture was filtered off and the catalyst was washed with dichloromethane and water in turn. The catalyst recycled was exploited seven more times without dismissing its catalytic aptitudes (Fig. 2).

The TEM image of the catalyst utilized in the Heck reaction after seven times of recyclability indicates that the morphology and size of the nanoparticles have remained almost intact (Fig. 1). This verifies that diaza-15-crown-5 is a very good *n*-donor ligand preventing aggregation and release of palladium nanoparticles.

CONCLUSIONS

In conclusion, this work shows that palladium nanoparticles can be stabilized efficiently by silica-bonded

n-propyl-diaza-15-crown-5 substrate. This catalyst can catalyse the Heck and the Suzuki reactions of both aryl bromides and chlorides efficiently with good to high yields. It could also be recovered and reused for several times without noticeable loss of activity.

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