

Modification of silica using piperazine for immobilization of palladium nanoparticles: a study of its catalytic activity as an efficient heterogeneous catalyst for Heck and Suzuki reactions

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Abstract An efficient heterogeneous palladium catalyst system has been developed based on immobilization of Pd nanoparticles on silica-bonded *N*-propylpiperazine (SBNPP) substrate. SBNPP substrate can stabilize the Pd nanoparticles effectively so that it can improve their stability against aggregation. Also, grafted piperazine species onto the silica backbone prevents the removing of Pd nanoparticles from the substrate surface. It seems that the high recyclable capability of Pd-SBNPP catalysts is resulted from these two characteristics. Transmission electron microscopy (TEM) of catalyst is shown the size of Pd nanoparticles in Pd-SBNPP average of 20 nm. Furthermore, X-ray photoelectron spectroscopy (XPS) of Pd-SBNPP is shown the presence of Pd(0) in the structure of this catalyst. Overall, TEM, XPS and XRD experiments strongly suggested that Pd nanoparticles were formed and immobilized on silica-functionalized piperazine. The catalytic activity of this catalyst was investigated in the Heck and Suzuki reactions. The catalyst could be recycled several times without appreciable loss in catalytic activity.

Keywords Heterogeneous palladium nanoparticles · Silica-bonded *N*-propylpiperazine · Heck reaction · Suzuki reaction · Aryl halides · Alkenes

Introduction

The wide application of metal-catalyzed reactions in academic studies and in the industry piqued the interest of many researchers to improve the synthetic methods for excellent performing of these processes [1–4]. Among many different existing metal-catalyzed strategies for C–C bond formations, palladium catalyzed protocols are mostly considered due to the unique characteristics of palladium [5–10]. Considering the importance of palladium reactions and the cost of palladium metal, different homogeneous and heterogeneous palladium catalyst systems have been developed [11–13]. In respect to the homogeneous catalysts, two different types of Pd catalytic systems are reported: (i) using palladium salt with ligands to be formed in situ Pd-complex in reaction condition, and (ii) using a pre-prepared complex of Pd. It is noteworthy that, in both systems often phosphorous and nitrogen-containing ligands have been used [14]. However, homogenous systems have two major problems; first, they cannot be reused and, therefore, they are not economical. Second, many ligands are toxic and air sensitive, so it is not a green and stable system [15]. In order to have the ability to recover homogeneous catalysts, a complex of palladium metal with the related ligands is deposited onto the surface of solid supports, thus forming heterogeneous catalysts [16, 17].

In the recent years, there is considerable attention on preparation of heterogeneous palladium catalyst based on nanometer scale palladium species [18, 19]. Palladium nanoparticles on a suitable support have the ability to be

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recoverable and ligand free green catalytic systems with improved catalyst characteristics [11, 17–21]. In heterogeneous Pd nanoparticle systems, the catalyst properties are improved due to high surface-to-volume ratio and consequently large fraction of metal atoms at the surface and also strong synergistic interaction between noble metal nanoparticles and the support [22–31]. Usually, palladium nanoparticle catalysts are prepared from a palladium salt on a substrate or stabilizer in the presence of a reducing agent [32, 33]. Steric, electrostatic, and electrosteric factors are responsible for the stabilization of PNPs during their synthesis.

Silica is an important solid surface for heterogeneous catalyst because of its abundant availability, high stability and the fact that organic groups can adjoin to the silica surface with strong connection to generate catalytic sites. With this view that silica gel surface is highly porous and can trap the palladium nanoparticles and hence stabilize them (prevent their aggregation), this substrate is used for supported palladium nanoparticles [25]. Laying the functional groups on the silica was shown more tendentious to stabilize the Pd nanoparticles and catalyst recovery [22–30].

Experimental

Chemicals and reagents

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 $^1\text{H-NMR}$ spectra we were using Bruker Avance (300 MHz or DRX 500 MHz) or Bruker Ultrashield (400 MHz) in pure deuterated CDCl_3 solvent with tetramethylsilane (TMS) as internal standards. X-ray diffraction (XRD, D8, Advance, Bruker, axs), 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 catalyst. Surface spectroscopy analyses of the catalyst were 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 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, NMR and the known compounds compared with those reported in literature [8–32].

Silica-bonded *N*-propylpiperazine (SBNPP)

To a magnetically stirred mixture of 3-chloropropylsilica (3 g) in xylene (110 mL), piperazine (1.3 mmol) was added and heated at 60 °C–70 °C, in presence of triethylamine as proton abstractor, under continuous stirring and a dry nitrogen atmosphere for 48 h. Then, the mixture was filtered and washed with dichloromethane (3×10 mL) and ethanol (3×10 mL). After drying in oven *N*-propylsilica piperazine (SBNPP) was obtained as white powder (3.4 g) [34].

Pd nanoparticles on silica-bonded *N*-propylpiperazine (PNP-SBNPP)

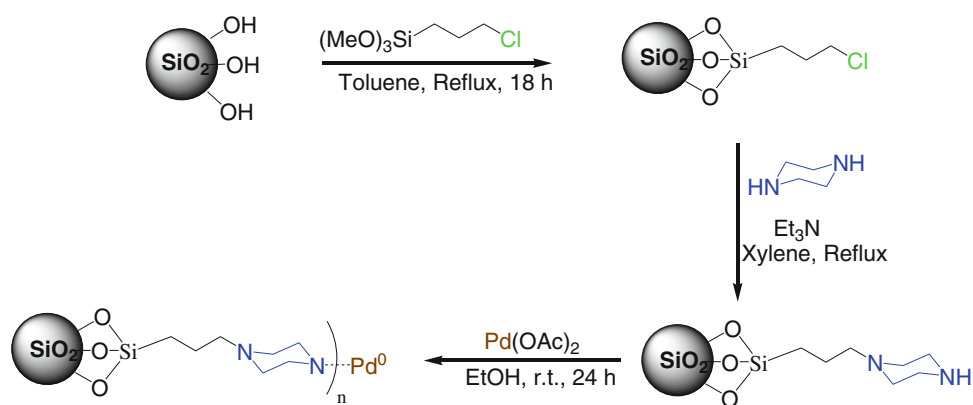
To a mixture of silica-bonded *N*-propylpiperazine (PNP-SBNPP) (1 g) in absolute ethanol (10 mL), palladium acetate (0.15 g, 0.67 mmol) was added and stirred 24 h at room temperature. Then, the mixture was filtered and washed with ethanol (3×10 mL). After drying in vacuum oven corresponding Pd nanoparticles on silica-bonded *N*-propylpiperazine (PNP-SBNPP) was obtained as dark solid (1.1 g).

General procedure for Heck reaction

To a mixture of aryl halide (1 mmol), alkene (1.2 mmol), and Na_2CO_3 (2.5 mmol) in 3 mL DMF, Pd nanoparticles on silica-bonded *N*-propylpiperazine (PNP-SBNPP) (0.035 g, 1.97 mol %) was added and heated on oil bath at 120 °C for the time specified in Table 2. 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 (2×10 mL) to separate catalyst. After extraction dichloromethane from water, the organic phase dried over Na_2SO_4 . Evaporation of the solvent gave products. For further purification if needed, the products passed through a short column of silica gel using *n*-hexane as eluent.

General procedure for Suzuki cross-coupling reaction

To a mixture of aryl halide (1 mmol), aryl boronic acid (1.2 mmol), and Na_2CO_3 (2.5 mmol) in 2 mL ethanol, Pd nanoparticles on silica-bonded *N*-propylpiperazine (PNP-SBNPP) (0.03 g, 1.69 mol %) was added and refluxed for the time specified in Table 3. 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) to separate catalyst. After extracting dichloromethane from water, the organic phase dried over Na_2SO_4 . Evaporation of the solvent gave products. For further purification if

Scheme 1 The synthetic route for preparation of PNP-SBNPP

needed, the products passed through a short column of silica gel using *n*-hexane as eluent.

Results and discussion

Catalyst preparation and characterization

As shown in Scheme 1, immobilized palladium nanoparticles on piperazine-modified silica (Pd-SBNPP) are prepared in a three-step process. First, activated silica [35] was reacted with 3-chloropropyl trimethoxysilane in refluxing toluene to produce 3-chloropropylsilica (3-CPS). Second, 3-CPS was treated with piperazine to generate the corresponding substrate. Finally, palladium acetate is reduced on SBNPP substrate using ethanol as green reducing agent [21] (Scheme 1).

The PNP-SBNPP catalysts were studied using the following techniques: FT-IR spectroscopy was used for the characterization of SBNPP (Fig. 1), transmission electron microscopy (TEM) (Fig. 2), scanning electron microscopy (SEM) (Fig. 4), powder X-ray diffraction (XRD) (Fig. 5), and X-ray photoelectron spectroscopy (XPS) (Fig. 6).

The FT-IR transmission spectrums of 3-chloropropylsilica, SBNPP, and PNP-SBNPP are shown in Fig. 1. The FT-IR of PNP-SBNPP the characteristic absorption at 3444.6 cm^{-1} is associated with the free -OH site on silica, while stretching frequency in 3419.6 cm^{-1} is related to free -OH in 3-chloropropylsilica. Stretching frequency in 2966.3 cm^{-1} related to C-H bond vibrations, strong bond in $1000\text{--}1200\text{ cm}^{-1}$ presumably because of stretching frequency C-O and C-N bonds that overlap with asymmetric stretching frequency of Si-O-Si bonds and two peaks in 1095.5 and 794.6 cm^{-1} related to asymmetric stretching and symmetric stretching of Si-O-Si bond, respectively, while stretching frequency in 1097.4 and 802.3 cm^{-1} is related to Si-O-Si in 3-chloropropylsilica.

TEM images of PNP-SBNPP catalyst (Fig. 2) show that the Pd nanoparticles with near spherical morphology are assembled onto the silica-bonded *N*-propylpiperazine

support with a relatively good monodispersity. Also, the histogram revealing the size distributions of Pd nanoparticles on SBNPP substrate is shown in Fig. 3 and is proposed according to the data obtained from the TEM image.

For Pd-SBNPP catalyst, the average sizes of Pd nanoparticles are obtained, 20 nm.

The microscopic features of the catalyst were observed with SEM (Fig. 4). In this figure, we can see morphology of the silica substrate. It can be seen that the Pd nanoparticles with a spherical morphology are well immobilized to the SBNPP substrates.

The crystalline structure of the PNP-SBNPP catalyst is displayed by the XRD pattern depicted in Fig. 5. The XRD

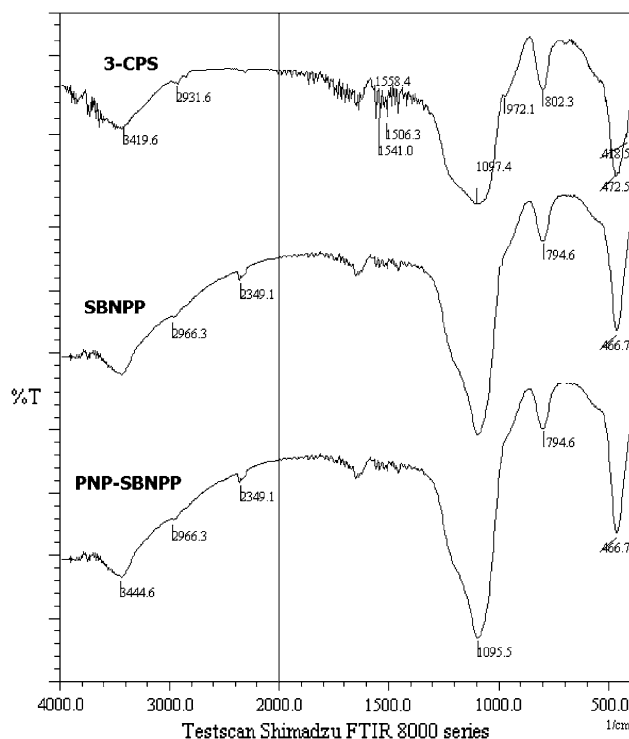


Fig. 1 FT-IR of 3-chloropropylsilica, SBNPP, and PNP-SBNPP for comparison

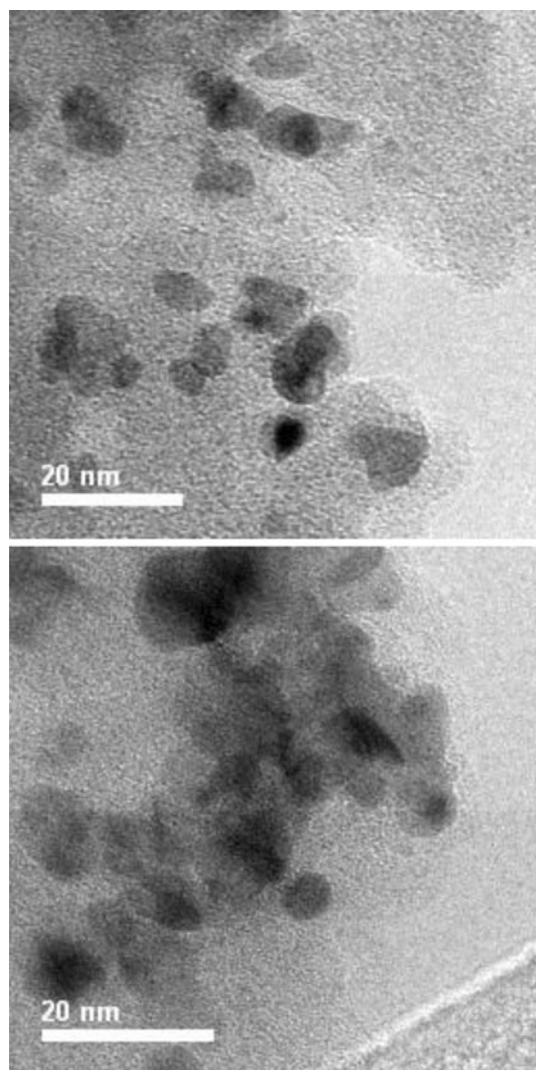


Fig. 2 Transmission electron microscopic (TEM), which show the image of Pd nanoparticle on SBNPP support

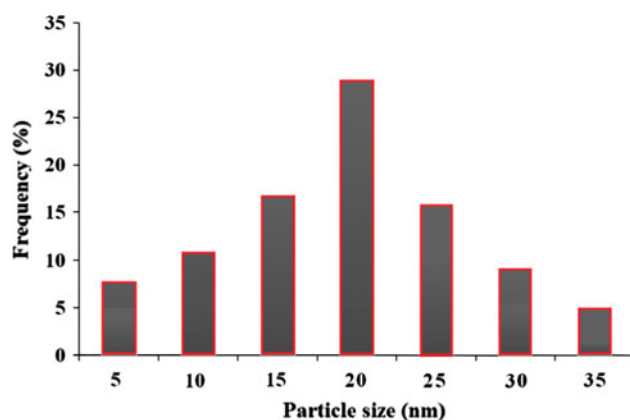


Fig. 3 Histogram representing the size distribution of Pd nanoparticles on SBNPP substrate

pattern of the PNP-SBNPP catalyst also shows palladium nanoparticles on the silica surface. The strongest peaks of the XRD pattern correspond to SiO_2 , and other peaks are indexed as the (111), (200), (220), and (311) planes of the palladium nanoparticle [35].

Figure 6 shows the X-ray photoelectron spectroscopy (XPS) spectrum of Pd ($3d$) envelope confirming the metallic Pd particles. XPS Pd ($3d_{5/2}$) and Pd ($3d_{3/2}$) peaks were observed at binding energy 335 and 340.1 eV, respectively. Such binding energy values are similar to that reported for Pd metals in the literature [35–37].

The BET surface area using nitrogen adsorption isotherms at the temperature of liquid nitrogen which gave the results of $a_{s,\text{BET}}$ $1.71 \text{ m}^2 \text{ g}^{-1}$ and the total pore volume $0.1653 \text{ cm}^3 \text{ g}^{-1}$ (see supplementary material).

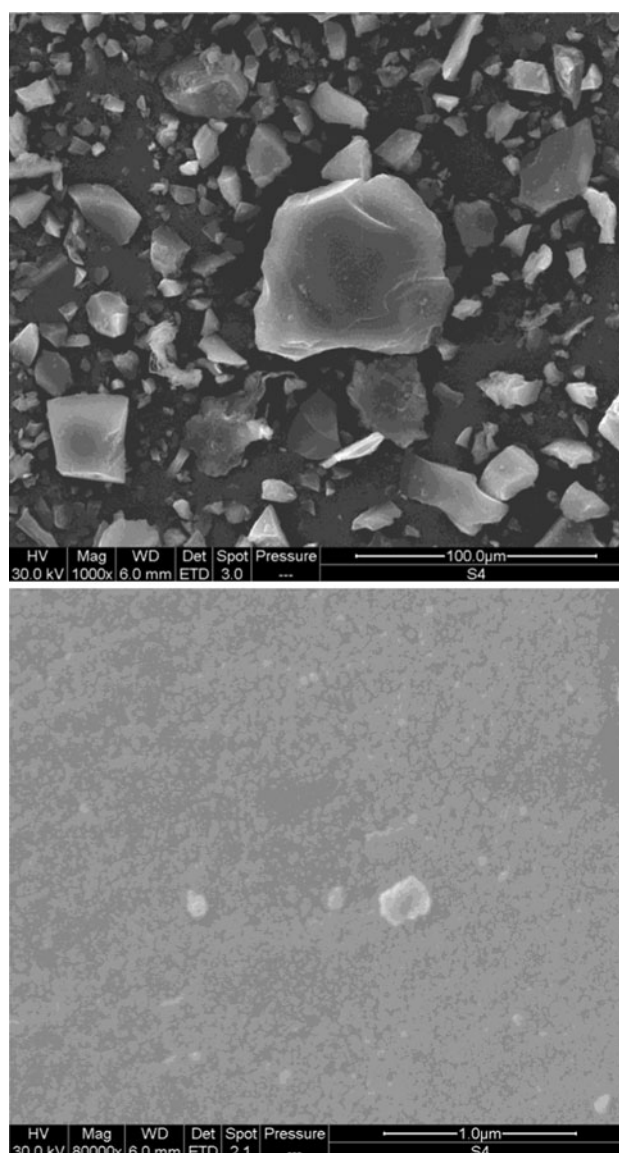


Fig. 4 Scanning electron microscopy (SEM) of PNP-SBNPP (magnifications: 1 mm, 100 μm and 1 μm)

Fig. 5 XRD of PNP-SBNPP

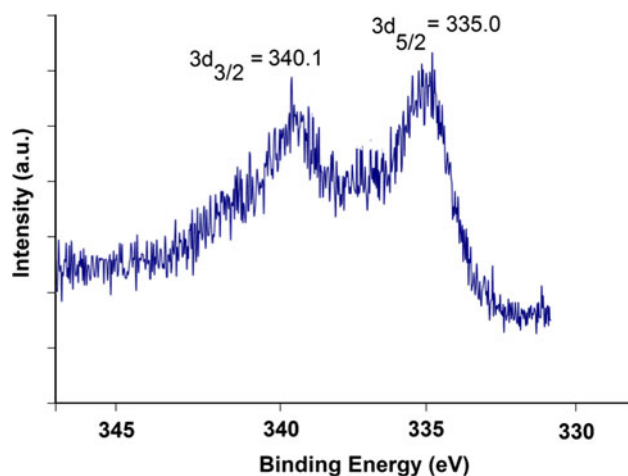
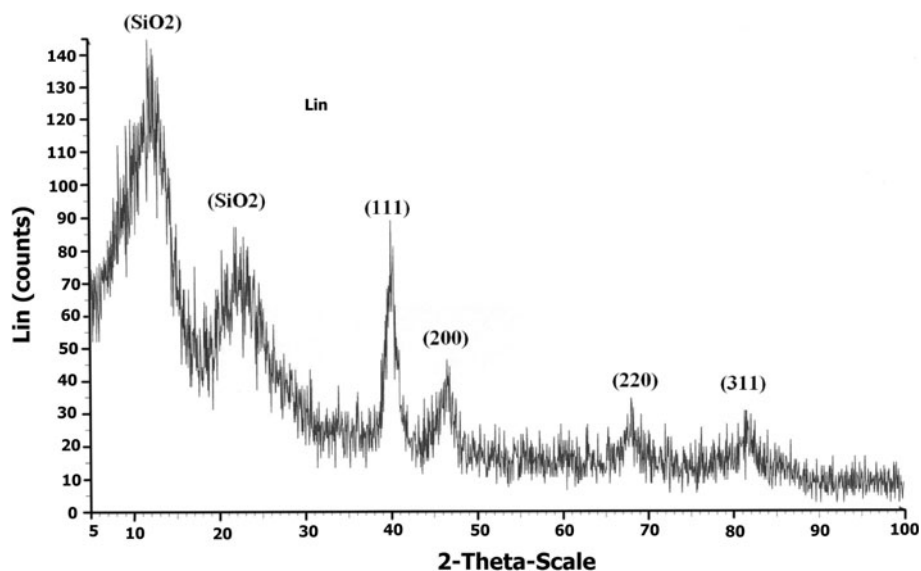


Fig. 6 The X-ray photoelectron spectroscopy (XPS) of PNP-SBNPP

To confirm the Pd content, the supported catalyst was treated with concentrated HCl and HNO₃ to digest the Pd species and then analyzed by ICP analysis. For this purpose, 100 mg of catalyst was digested in 50 mL of HNO₃ (10 % w/w) and then atomic emission of solution was determined which resulted in a Pd content about 6.0 % w/w.

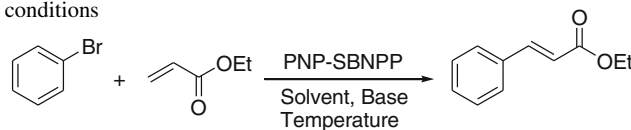
After characterization of catalyst, its catalytic activity is tested in two important cross-coupling reactions: Heck and Suzuki.

Pd-SBNPP catalyzed reactions

Heck reaction

We tested various conditions to optimize the amount of PNP-SBNPP catalyst on the Heck reaction between bromobenzene and ethyl acrylate (Table 1). This reaction does

Table 1 Optimization reaction between bromobenzene and ethyl acrylate in the presence of PNP-SBNPP as a catalyst at various conditions

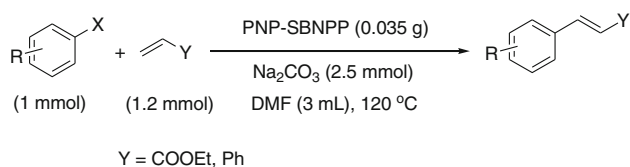


Entry	Solvent	Base	Catalyst loading (g)	Temp (°C)	Time (h)	Yield ^a %
1	DMF	Na ₂ CO ₃	0.0	120	24	0
2	DMF	Na ₂ CO ₃	0.01	120	24	60
3	DMF	Na ₂ CO ₃	0.035	120	8	90
4	DMF	Na ₂ CO ₃	0.05	120	4	89
5	DMF	K ₂ CO ₃	0.035	120	8	70
6	DMF	Cs ₂ CO ₃	0.035	120	8	30
7	DMF	Et ₃ N	0.035	120	8	10
8	Toluene	Na ₂ CO ₃	0.035	Reflux	10	80
9	THF	Na ₂ CO ₃	0.035	Reflux	10	30
10	H ₂ O	Na ₂ CO ₃	0.035	Reflux	10	Trace
11	CH ₃ CN	Na ₂ CO ₃	0.01	Reflux	10	54
12	DMF	Na ₂ CO ₃	0.035	140	10	77
13	DMF	Na ₂ CO ₃	0.035	80	48	55

Reaction conditions: bromobenzene (1 mmol), ethyl acrylate (1.2 mmol) and base (2.5 mmol) in solvent (3 mL)

^a Isolated yield

not take place in the absence of catalyst even after 24 h at 120 °C (Table 1, entry 1). The optimized amount of catalyst was 0.035 g (1.97 mol % of Pd). By decreasing the catalyst to 0.01 g (0.56 mol % of Pd), the yield of product decreased and the time of reaction was increased (Table 1, entry 2), while the increase of catalyst to 0.05 g (2.82 mol % of Pd) did not have more effect on the



Scheme 2 Investigation the Heck reaction catalyzed by PNP-SBNPP

reaction yield (Table 1, entry 4). In addition, different conditions such as solvent, base and temperature were optimized and the result was shown in Table 1.

Thus, the following conditions were selected; aryl halide (1 mmol), ethyl acrylate (1.2 mmol), Na_2CO_3 (2.5 mmol), and PNP-SBNPP catalyst (0.035 g, 1.97 mol %) in 3 mL DMF at 120 °C (Scheme 2 and Table 2).

Table 2 The reaction of ethyl acrylate or styrene with aryl halides in the presence of PNP-SBNPP as catalyst (Heck reaction) at 120 °C

Entry	Aryl halide	Y	Product	Time (h)	Yield (%) ^a
1		COOEt		8	90
2		COOEt		15	62
3		COOEt		20	45
4		COOEt		8	90
5		COOEt		16	50
6		Ph		15	78
7		Ph		24	54
8		Ph		15	84
9		Ph		15	75
10		Ph		24	70
11		Ph		24	45
12		Ph		24	48

Reaction conditions: aryl halide (1 mmol), alkene (1.2 mmol), Na_2CO_3 (2.5 mmol), catalyst (0.035 g), DMF (3 mL) at 120 °C

^a Isolated yield

The generality of this protocol was applied for coupling of various alkenes (including ethyl acrylate and styrene derivatives) with aryl halides (Table 2).

According to Table 2, ethyl acrylate was found to couple smoothly with bromobenzene and chlorobenzene providing a moderate yield of the desired product (entries 1 and 2). The electron-donating groups on the aryl ring decreased the reaction rate as well as the yield of product (Table 2, entry 3). Sterically hindered mesityl bromide was treated with ethyl acrylate under optimized conditions providing 50 % yield of the desired product (Table 2, entry 5). Bromobenzene and chlorobenzene derivatives were also successfully coupled with styrene and the electron-withdrawing and electron-donating groups on the aryl ring with good- to high-yields (Table 2, entries 6–12). It should be noted that all products obtained exclusively with an (*E*)-configuration.

Suzuki reaction

The scope of this methodology was extended to the Suzuki reaction. Initially the reaction of bromobenzene with phenylboronic acid was studied as a model reaction in the presence of PNP-SBNPP as catalyst. The optimized conditions for Suzuki reaction were as follows: aryl halide (1 mmol), aryl boronic acid (1.2 mmol), Na₂CO₃ (2.5 mmol), PNP-SBNPP (0.03 g, 1.69 mol %) in 2 mL of ethanol at reflux conditions. The efficiency of this system was further extended for coupling of various aryl halides having different steric and electronic properties with phenylboronic acid. The results are summarized in Table 3. Phenylboronic acid was found to couple smoothly with

bromobenzene providing an excellent yield (91 %) of desired product. The reaction also worked well with less reactive chlorobenzene giving 81 % yield. As it was clearly shown in Table 3, the GC-yield of by-product confirms this point that these catalyst systems are more effective, and so homocoupling of boronic acid was obtained poorly.

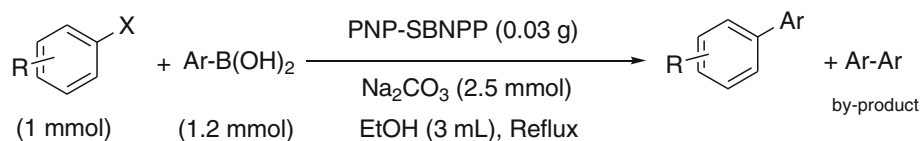
Electron-withdrawing groups such as nitro, and donating groups such as methyl, methoxy, and methylthio were well tolerated under the present catalytic systems (Table 3, entries 3–4, 5–8). 2-iodothiophene and 4-bromoisoquinoline were reacted with phenyl boronic acid in the presence of PNP-SBNPP catalyst under optimized conditions to give the corresponding product in high yield (Table 3, entries 9 and 10).

Recycling of the PNP-SBNPP catalyst for the Heck and Suzuki reactions

The possibility of recycling the PNP-SBNPP catalyst was examined using the reaction of bromobenzene with ethyl acrylate under optimized conditions. Upon completion, the reaction mixture was filtered and the catalyst was washed with dichloromethane. The recycled catalyst could be reused five times without any treatment (Table 4).

The possibility of recycling the PNP-SBNPP catalyst in Suzuki reaction was examined using the reaction of 4-nitro-bromobenzene with phenylboronic acid under optimized conditions. When the reaction was completed (confirmed by TLC), the reaction mixture was filtered and the catalyst was washed with dichloromethane. The recycled catalyst could be reused six times without any treatment (Table 5).

Table 3 The reaction of phenyl boronic acid or 4-ethylphenyl boronic acid with aryl halides in the presence of PNP-SBNPP as catalyst. Reaction conditions: aryl halide (1 mmol), boronic acid (1.2 mmol), Na₂CO₃ (2.5 mmol), water (2 mL) at 80 °C



Entry	X	R	Ar	Time/h	Yield (%) ^a	Yield of by-product (%)
1	Br	H	Ph	1	91	–
2	Cl	H	Ph	4	81	–
3	Br	4-NO ₂	Ph	1	92	–
4	Cl	4-NO ₂	Ph	8	73	8
5	Cl	4-OMe	Ph	8	62	18
6	Cl	4-Me	Ph	5	68	15
7	Br	4-SMe	Ph	4	84	8
8	Cl	4-OMe	4-Et-Ph	8	61	10
9	2-Iodothiophene	–	Ph	0.8	87	5
10	4-Bromoisoquinoline	–	Ph	1.5	85	5

^a Isolated yield

Table 4 Reusability of the PNP–SBNPP catalyst in the Heck reaction

Entry	Yield of product (%)	Recovery of PNP–SBNPP (%)
fresh	90	>99
1	89	99
2	87	98
3	87	97
4	86	97
5	85	96

Reaction conditions: PNP–SBNPP (0.07 g), Na₂CO₃ (5.0 mmol), DMF (5 mL), bromobenzene (2.0 mmol) and ethyl acrylate (2.4 mmol)

Table 5 Reusability of the PNP–SBNPP catalyst in the Suzuki reaction of bromobenzene and phenyl boronic acid

Entry	Yield of product (%)	Recovery of PNP–SBNPP (%)
fresh	91	>99
1	90	99
2	90	99
3	89	98
4	88	97
5	87	97
6	87	96

Reaction conditions: PNP–SBNPP (0.06 g), Na₂CO₃ (5.0 mmol), EtOH (5 mL), bromobenzene (2.0 mmol) and ethyl acrylate (2.4 mmol)

Conclusions

In conclusion, this work shows that palladium nanoparticles can be stabilized efficiently by silica-bonded *N*-propylpiperazine substrate. These materials can be prepared by simple operation from commercially available and relatively cheap starting materials. The XRD, TEM, SEM, and size analyzer confirmed the palladium nanoparticles are immobilized on SBNPP substrate. PNP–SBNPP efficiently catalyzed the Heck and Suzuki reactions of both aryl bromides and chlorides with good to high yields. This catalyst could also be recovered and reused for several times without noticeable loss of reactivity.

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