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ARTICLE

Palladium nanoparticle catalyzed *aryl-amine* coupling reaction: High performance of aryl and pyridyl chlorides as the coupling partner

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Carbon nitride (CN) supported nanosized palladium particles, Pd-CN, have been found to be an active catalyst system for the amination of aryl and pyridyl chloride moieties in presence of dialkyl amine under mild reaction condition. The recyclability study of the reaction shows the stable performance of the catalyst without the significant loss of catalytic activity for the couple of cycles.

Construction of aryl-amine containing molecules through transition metal catalyzed cross coupling reaction has been received considerable attention due to their applicability in diverse branches of science and technology.[1, 2] The palladium-catalyzed cross-coupling reaction of the aryl halides and the amines for the synthesis of arylamine molecule was initially reported by Migita, whereas, the major breakthrough in this field was attributed by Buchwald and Hartwig.[3-5]

The development of improved ligands and catalysts remained a major focus to address general and reliable applicability of this protocol.[6] Phosphine containing symmetrical monodentate ligand and the ligands with different alkyl substituents has been reported for the title reaction.[7] Reports are also available on bidentate phosphine, sterically hindered and electron-rich phosphines and non-phosphine ligands for the effective and successful implementation of the reactions with wide range of substrate scope.[8] Synthesis of palladium catalysts has been reported using various phosphines and *N*-heterocyclic carbene ligands for the aryl-amine coupling reaction.[9] Besides that varieties of palladacycles,[10] pyridine-containing palladium complexes[11] and π-allyl palladium complexes[12] has been used for the rapid generation of active catalyst in the reaction mixture for the successful demonstration of the title reaction. Copper based material also showed the catalytic role for construction of arylamine moiety. Several classes of mono- and bidentate chelators, such as, diamines[13], diols[14], amino acids and alcohols[15] are also found as effective catalytic system for construction of arylamine moiety.

Regardless of these well versed and reliable progress for the aryl-amines cross coupling reaction in presence of homogeneous transition metal catalyst, few major drawbacks, such as, regeneration and recyclability of the catalyst, contamination of metal ions in the product, tedious ligand synthesis protocol, moisture sensitivity of the catalyst,[16] causes severe limitation for the success of the reaction. Apart from that, the aggregation and precipitation of metal catalyst in homogeneous catalysis system causes the poor performance of the reaction and in order to avoid that phenomenon a heterogeneous route could be an attractive solution to address these existing problems.

Due to the interesting and versatile chemical properties, palladium nanoparticle have been implied in a diverse range of cross coupling reaction. Due to the interesting and versatile chemical properties, palladium nanoparticle have been implied in a diverse range of cross coupling reaction. It has been reported that nafion-graphene composite film Pd nanoparticles showed C-C and C-N cross-coupling reaction.[17] Zinc oxide supported palladium nanoparticle catalyzed C-O and C-N bond formation has been evidenced with satisfactory amount of yields.[18] Report has also been published on the Pd catalyzed Buchwald-Hartwig C-N cross coupling reaction on silica-starch substrate with excellent recycling performance.[19] A tandem reaction of C-H halogenation and cross-coupling (C-N, C-C, and C-S bond formation) was successfully established using controlled oxidation of metallic Pd, where the role of the palladium was as a catalyst.[20] Application of palladium nanoparticle is also evident in enantioselective allylic alkylation[21] and hydrogenation[22] reactions. Two major factors effecting the catalytic activity of palladium nanoparticle are particle size and the presence of active atom on solid support of composite materials.[23] Mesoporous layered structured carbon nitride with high chemical and thermal stability could be a promising support material for the nanocatalysts for the heterogeneous catalysis process where the nitrogen moiety could give the additional stability of the nanoparticles. The recent literatures show the unique role of carbon nitride as a support material of the metal nanoparticles for heterogeneous oxidation and hydrogenation reactions.[24] The catalyst made of Pd nanoparticles supported on a mesoporous carbon nitride was shown to be highly active for the selective formation of cyclohexanone from phenol under atmospheric pressure of hydrogen in aqueous media.[25] An identical system also showed excellent catalytic performance for the selective hydrogenation of nitrogen heterocycles where quinoline is converted to tetrahydroquinoline with high selectivity under mild temperature and pressure (hydrogen) condition.[26]. Hydrogenation of nitriles is one of the most common methods to prepare amines and the carbon nitride supported palladium was employed for the chemical transformation of butyronitrile to tri-n-butylamine.[27] Recent publication described the hydrogenation of nitrophenol by mesoporous carbon nitride supported noble metal catalysts. The ultrafine noble metal nanoparticles were homogeneously distributed inside the meso-channels and all the catalysts demonstrated high conversions.[28] Carbon nitride supported gold

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nanoparticle was demonstrated as an effective catalyst for the transformation from cyclohexane to cyclohexanone with 100% selectivity.[29]

In connection with our ongoing research on the development of effective catalysts for synthetic organic transformations,[30] we have also found the possibility of using carbon nitride as the support material for the various reactions. Carbon nitride supported palladium was used as an active catalyst for the mono arylation of imidazo [1, 2-*a*] pyridine and 1, 2-dimethyl imidazole and also for the reduction of aromatic nitro-compounds.[31] Copper catalyzed *N*-arylation of hetero-aromatic compounds[32] and light-induced triazole synthesis[33] were also reported and proved the versatility of the carbon nitride as a support material.

In this manuscript we like to report the cross coupling reaction for the amination of aryl and pyridyl chloride moieties using dialkylamine under the mild reaction condition using carbon nitride supported palladium nanoparticles as a catalyst with the scope of recyclability of the catalyst.

The synthesis of polymeric form of carbon nitride (CN) and the carbon nitride supported metal nanoparticles (M-CN, where, M = Pd and Cu) has been previously reported elsewhere.[31, 33] The detail synthesis method, of the carbon nitride and the carbon nitride supported palladium nanoparticles, has also been described in the supplementary document (page: S8). The electron microscopic image shows a small area of the synthesized carbon nitride (figure 1A) and carbon nitride supported palladium nanoparticles (dark spots), where the particles are dispersed on the CN support within the size rage of 5-20 nm (figure 1B).

Figure: 1

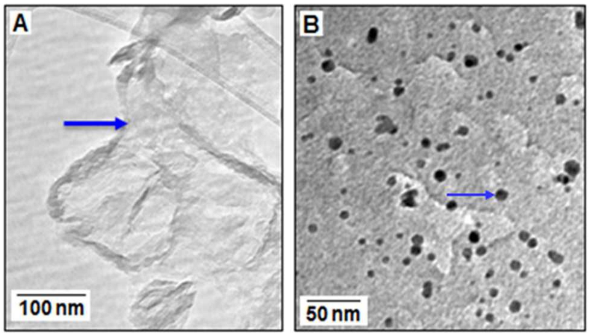

Figure 1: TEM image of the carbon nitride and carbon nitride supported palladium nanoparticles (indicated by the arrows).

In this current experiment, aryl or pyridyl chloride (1 mmol), aryl dialkylamine (1.0 mmol), CF_3SO_3Li (234 mg, 1.5 mmol), and 5.0 mg of Pd-CN (5.0 wt% of Pd) catalyst were added in 2 mL of N-Methyl-2-pyrrolidone (NMP).

To find out the optimum reaction condition for aryl and amine coupling reaction, 1-chloro-4-nitrobenzene (**1a**) and piperidine (**2d**) was chosen as coupling partners [table S1: supporting information]. Initially we focused to screen the performance of various bases (1.5 equivalent of each), such as, K_2CO_3, Cs_2CO_3, KOAc, K_3PO_4, KO^{t}Bu, Et_3N and CF_3SO_3Li [entry: 1-6 and 7-10], for the suitability of the above reaction. Among them, CF_3SO_3Li showed the best performance and produces the yield of 95% of the coupling product 1-(4-nitrophenyl) piperidine (**3ad**). We also have optimize the reaction condition by using different solvent system, such as, N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidine (NMP) and tetrahydrofuran (THF) where we found that the NMP served as the best solvent for the coupling reaction between 1-chloro-4-nitrobenzene and piperidine [entry: 9 and 13-15]. An optimum temperature of 80^{o}C was selected for the reaction because further increase or decrease (not included in the table) of temperature does not have any positive impact on the yield of the reaction [entry: 7-9]. We also found that the quantity of 5 mg of Pd-CN with 5 wt% of Pd loading was ideal for the reaction [entry: 8-10]. The optimization study also showed the better performance of Pd-CN system as compared with the $Pd(OAc)_2$ and $Pd(PPh_3)_4$ catalyst [entry: 11, 12].

Based on the above optimized conditions we were interested to check the general applicability of the title reaction with a set of aryl or pyridyl chloride and different dialkyl substituted amine compounds (Table: 1). When 1-chloro-4-nitrobenzene (**1a**) was used as the as the coupling partner for wide range of dialkyl compounds such as diethylamine (**2a**), dibutylamine (**2b**), pyrrolidine (**2c**) and piperidine (**2d**), the corresponding products *N,N*-diethyl-4-nitroaniline (**3aa**), *N,N*-dibutyl-4-nitroaniline (**3ab**), 1-(4-nitrophenyl)pyrrolidine (**3ac**) and 1-(4-nitrophenyl)piperidine (**3ad**) were obtained with an isolated yield of 75%, 88%, 93% and 95%, respectively. The above mentioned dialkyl compounds also produced the aryl-amine coupled products of *N,N*-diethylpyridin-2-amine (**3ba**), *N,N*-dibutylpyridin-2-amine (**3bb**), 2-(pyrrolidin-1-yl)pyridine (**3bc**) and 2-(piperidin-1-yl)pyridine (**3bd**), with an isolated yield of 83, 91, 92 and 94%, respectively, when combined with 2-chloropyridine (**1b**) in the presence of Pd-CN catalyst. The nitro-substituted pyridyl chloride, 2-chloro-3-nitropyridine (**1c**), was also sensitive for the coupling reaction with the above dialkyl compounds and forms *N,N*-diethyl-3-nitropyridin-2-amine (**3ca**), *N,N*-dibutyl-3-nitropyridin-2-amine (**3cb**), 3-nitro-2-(pyrrolidin-1-yl)pyridine (**3cc**) and 3-nitro-2-(piperidin-1-yl)pyridine (**3cd**) with the individual yield of 79, 83, 89 and 87%, respectively.

The title reaction was further extended for 2, 5-dichloropyridine (**1d**), as the coupling partner, with the dialkyl compounds (**2, a-d**) and resulted to the formation of 5-chloro-*N,N*-diethylpyridin-2-amine (**3da**), *N,N*-dibutyl-5-chloropyridin-2-amine (**3db**), 5-chloro-2-(pyrrolidin-1-yl)pyridine (**3dc**) and 5-chloro-2-(piperidin-1-yl)pyridine (**3dd**) successfully with the regiospecific mono-amination at the C-2 position leaving the chloro-functionality (C-5) undisturbed. In a similar fashion, 2-chloro-4-nitropyridine (**1e**) also underwent the coupling reactions with diethylamine (**2a**), dibutylamine (**2b**), pyrrolidine (**2c**) and piperidine (**2d**) with the formation of the alkyl-amine coupling products, such as, *N,N*-diethyl-4-nitropyridin-2-amine (**3ea**), *N,N*-dibutyl-4-nitropyridin-2-amine (**3eb**), 4-nitro-2-(pyrrolidin-1-yl)pyridine (**3ec**) and 4-nitro-2-(piperidin-1-yl)pyridine (**3ed**), respectively, and more than 90% yield of the coupling products were achieved when carbon nitride supported palladium was used as a catalyst. A yield comparison of present work with few earlier reported similar compounds is also available as a ready reference in the supplementary document, page: S3, table: S2.

The design and synthesis of recoverable catalysts is highly challenging. Recyclability of the catalyst is one of the important parameter of heterogeneous catalysis to reduce the chemical waste and make the system economically viable. In this current report, the recyclability study was performed for the aryl-amine coupling between the reactants 1-chloro-4-nitrobenzene (**1a**) and piperidine (**2d**), with the formation of 1-(4-nitrophenyl) piperidine (**3ad**) as a product, using Pd-CN as catalyst. By maintaining the identical optimized reaction conditions, the amount of two substrates and other reagents have been increased ten times so that a simultaneous study of recyclability of the catalyst and scaling up of the reaction could be performed.

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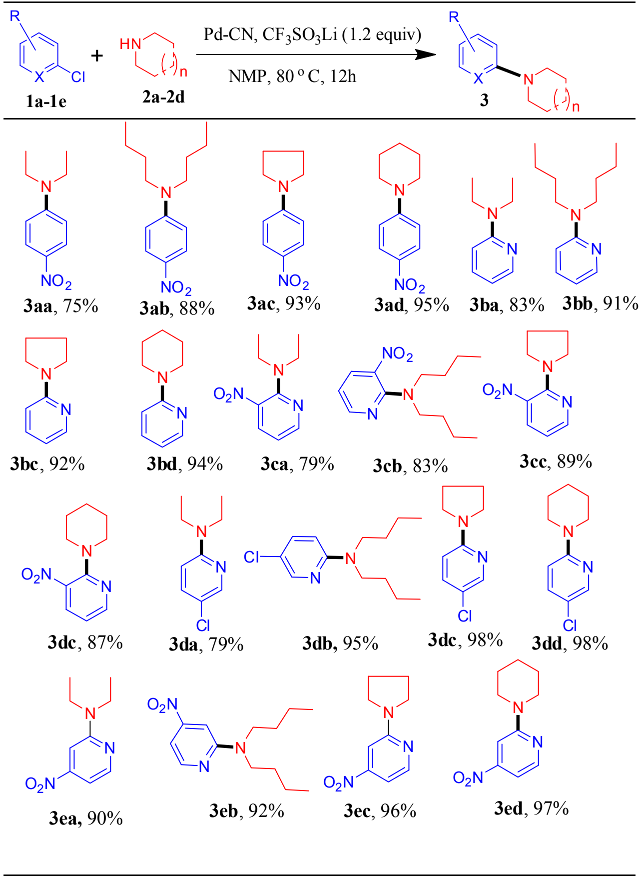
Table 1: Synthesized aryl-amine coupled product using the Pd-CN catalyst. [a, b]



(a) Reaction conditions: aryl or pyridyl chloride, **1,** (1.0 mmol), dialkylamino, **2,** (1.0 mmol), CF_3SO_3Li (234 mg, 1.5 mmol), Pd-CN catalyst (5 mg, 5 wt% of Pd loading) and NMP (2mL). (b) Isolated yield.

An isolated yield of 95% of the product (**3ad**) was achieved after completion of the first cycle. At the end of sixth cycle a moderate deactivation of reaction with an isolated yield of 83% of the product was noticed. After the completion of every cycle, the catalyst was recovered by filtration technique and used for next cycle. The graphical representation (figure 2A) shows the recycling performance of the catalyst in terms of product yield (%) as a function of cycle number. The gradual decrease of the yield in each cycle could be associated with the loss of the catalyst during the filtration and washing process. It is also important to mention that the loss of catalyst (palladium species) due to the leaching process was not observed in this study as the inductively coupled plasma mass spectrometry (ICP-MS) analysis of the filtrate, collected during the recyclability study, did not record any palladium species within the detection limit of the instrument and that could be due the presence of intercalated structure and amine functionality of the support which makes the support-particle binding system more stronger.[33] At the end of the sixth cycle the recovered catalyst was characterized by transmission electron microscopy technique and a significant amount of particle enlargement, within the range of 14-35 nm, was observed (figure 2B). The enlargement of the particles could be explained in terms of Ostwald ripening effect,[34] a growth mechanism phenomenon, for which the effective surface area or the active sites of the catalyst was decreased and that could be the other reason for the deactivation of the catalyst over the cycles.

The kinetics of aryl-amine coupling between the reactants 1-chloro-4-nitrobenzene (**1a**) and piperidine (**2d**) revealed the response of the reaction under the influence of catalyst. The graphical representation (figure 2C), percentage of conversion (from reactant to product, **3ad**) as a function of time (for the period of 12h), showed that in the first 2h the rate of the reaction was very slow and could be considered as the induction period for the reaction. A faster and steady rate of product formation was noticed within the time range between 4-7h. At the end of eighth hour, slightly higher than 80% of product was achieved. For the last four hours, a fatigue behaviour in the kinetic graph was noticed which indicates the passivation of the catalyst due to the blocking of active sites by the deposition of solid product formed during the reaction.

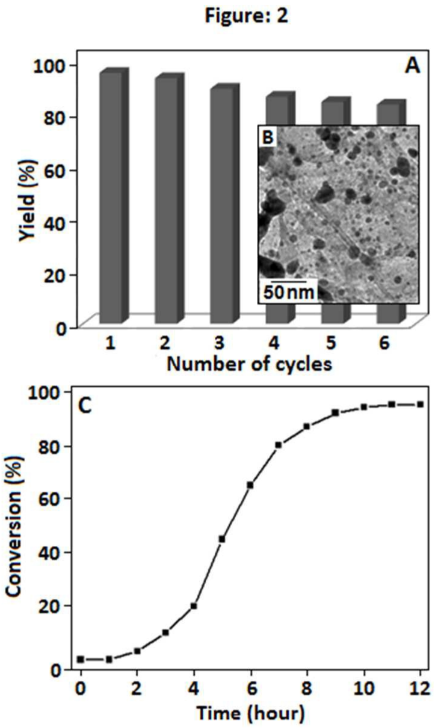


Figure 2: (A) The histogram from the recyclability study of the Pd-CN catalyst system. (B) The TEM image of the used catalyst (Pd-CN), at the end of the sixth cycle. (C) The graphical representation of the kinetic study for the aryl-amine coupling reaction as a function of time.

The schematic diagram (scheme: S1, supporting information) shows the synthesis route for the formation of Pd-CN **(A)**. The catalyst combines with aryl or pyridyl chloride to generate the intermediate complex **(B)** due to oxidative addition. On the other hand, the alkyl amine molecule (B′) forms the lithium salt of the corresponding amine (B′′) due to the acid-base reaction with lithium trifluoro-methanesulfonate with the release of trifluoro-methanesulfonic acid. In the next step, lithium salt of amine (B′′) due to transmetallation reaction forms the intermediate **(C)** with the elimination of lithium chloride salt. Further reductive elimination resulted to the aryl-amine cross coupling product **(D)** and regenerate the active metallic palladium species for the next cycle. It is also important to mention that in the current experiment we

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have used carbon nitride supported metallic palladium as the catalyst system but according the mechanism the oxidative addition with aryl or pyridyl chloride resulted the formation of palladium (II) species (scheme: S1, supporting information, step B). So it suggests that the real catalyst species is only Pd (II), which is a single site catalysis process,[35] for the current aryl-amine bond formation reaction. The oxidative transformation process of Pd (0) to Pd (II) could be the reason for the relatively longer induction period (figure 2C).

The reactivity of the less reactive aryl or pyridyl chloride moieties in the presence of a catalyst is highly desirable from the commercial point of view. In this current work, the catalyst, carbon nitride supported palladium nanoparticles, used for the aryl-amine coupling reaction, was synthesized in a two-step methodology using the precursors of urea and potassium tetrachloropalladate (II), respectively. The catalyst also has shown its potential for the recyclability of the title coupling reaction without a significant loss of catalytic activity.

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TEXT:

Carbon nitride supported Pd nanoparticle catalyzed C-N cross coupling reaction

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