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Diamines as interparticle linkers for silica-titania supported Proceeding Discover bimetallic nanoparticles in Chan-Lam and Suzuki cross-coupling reactions

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Keywords: Pd-Cu nanoparticles; silica-titania; heterogeneous catalysis; amines; Suzuki coupling; Chan-Lam cross-coupling.

Abstract

A series of highly efficient amine functionalized SiO₂-TiO₂ supported bimetallic PdCu catalysts with varied metal composition have been synthesized. Ethane-1,2-diamine, butane-1,4-diamine and hexane-1,6-diamine were employed as interparticle linkers for amine functionalization of a SiO₂-TiO₂ support material so as to study the effect of pendant chain length on stabilization and immobilization of bimetallic nanoparticles. The shortest carbon chain length on the support provided the best results which may be due to the trapping of metal nanoparticles more efficiently by the basic nitrogen sites. The catalytic activities of these materials were evaluated for C–N and C–C coupling reactions. The most active catalyst, Pd₁Cu₁@12DA-STS was characterized by various techniques including SEM, HR-TEM, ICP-AES, XRD, FTIR, EDX, CHN analysis and TGA studies. Moreover, the synthesized catalyst was found to be recyclable for up to five runs without loss of significant activity.

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Introduction

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Bimetallic nanocatalysis has emerged as a spectacular and exciting field of catalysis since it offers a way to modify the catalytic properties of metals. Several studies have demonstrated that bimetallic nanoparticles can go beyond their monometallic counterparts by exhibiting a significantly higher catalytic performance in terms of activity, selectivity and stability¹. Heterogeneous bimetallic catalysts^{2,3} are highly distinctive and offer incredible opportunities for tuning catalytic activity by controlling the size, shape, chemical composition and dispersity of metal nanoparticles^{4,5}. Their enhanced catalytic behaviour is attributed to the synergistic effect that exists between the two metals⁶. The heterogeneous bimetallic catalysts, for instance Ir-Au/TiO₂⁷, Pd-Cu/TiO₂–CeO₂⁸, Cu-Ni/AC⁹, Pd-Ni/ZrO₂¹⁰ and many others have recently been explored for their multifunctional applications. Though there has been a tremendous progress in the field of bimetallic catalysis, still there is much scope for the improvement of the current strategies and techniques to arrive at the best catalytic system in terms of activity and selectivity¹¹. Various organic or inorganic supports such as carbon¹², graphene¹³, metal oxides^{14,15}, zeolites^{16,17}, EDTA¹⁸ are being used to immobilize bimetallic nanoparticles for their higher stability, dispersion and stabilization¹⁹. The combination of two nanoscale inorganic moieties have gained much attention as they yield a composite with high surface area and desirable porosities to improve their catalytic performance^{20,21}. Abundantly available silica being highly stable can trap the metal nanoparticles easily and hence is widely used as a catalyst support²². But the surface of the silica cannot hold metal nanoparticles for long when used in a reaction, thereby decreasing the activity of the catalyst after even a small number of runs²³. Recently, titania, has emerged as a feasible support for the immobilization of metal nanoparticles due to its good biological compatibility, non-toxicity, cost-effectiveness and easy preparation^{7, 24}. Studies have been devoted to the synthesis of silica-titania composites with well-controlled texture as they have considerable potential for applications in chemical industry and biomedical technology^{25, 26}.

Although, SiO₂-TiO₂ composite shows improved properties, it suffers from some disadvantages such as leaching of metal nanoparticles and thus, decreases the likelihood of making the catalyst reusable. Recently, different binding agents such as phosphine, imine, acetylacetonate, oleic acid, L-dopa²⁷ and amine moieties²⁸ have been reported which stabilizes the metal nanoparticles against aggregation and also enhance their catalytic properties²⁹. A strong interaction between metal nanoparticles and the amine functionalized

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support is believed to account for the enhanced stability of these catalyst materials³⁰ In View Article Online present work, bimetallic heterogeneous catalytic systems based on Pd-Cu nanoparticles supported onto amine functionalized silica-titania have been developed. The developed catalysts were tested for Chan-Lam and Suzuki cross-coupling reactions. Earlier, there are reports in literature where Chan-Lam process³¹⁻³³ of C-N bond formation has been carried out using different copper salts in the presence of various ligands, which include square $[Cu(DMAP)4I]I^{34}$, nanoparticles³⁵, pyramidal Cu-doped CoFe₂O₄ Copper iminoarylsulfonate complexes³⁶, Ni- and Cu-based Catalysts³⁷ etc. We intend to report a bimetallic heterogeneous catalytic system where different diamines were used as interparticle linker and incorporated onto silica-titania support in order to study the effect of pendant chain length on stabilization and immobilization of bimetallic nanoparticles. Pd and Cu nanoparticles with varied metal composition were immobilized onto the support in order to investigate the effect of Pd/Cu ratio on the stability of the catalytic system. Out of the various catalysts, Pd₁Cu₁@12DA-STS showed superior activity for Chan-Lam and Suzuki cross-coupling reactions and was fully characterized by FT-IR, TGA, SEM, HR-TEM, CHN, EDX, ICP-AES, XRD and XPS.

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Experimental

Materials and Characterization

All the chemicals used were purchased from Aldrich Chemical Company or Merck. Silca gel (Merck grade 7734, pore size 60 °A, 70-230 mesh) was used in the present study. Perkin-Elmer FTIR spectrophotometer was used to record the FTIR spectra of the samples. The ¹H and ¹³C NMR data were recorded in CDCl₃ on Bruker Avance III (400 and 100 MHz) and mass spectral data on Bruker Esquires 3000 (ESI). X-ray diffratograms (XRD) were recorded in 2 theta range of 10–80° on a Bruker AXSDB X-ray diffractometer using Cu Kα radiations. BET (Brunauer-Emmett-Teller) surface area was determined from N₂ adsorption-desorption isotherms using Autosorb-IQ MP analyzer. XPS spectra of the catalyst were recorded on KRATOS ESCA model AXIS 165 (Resolution). TGA was recorded on Perkin Elmer, Diamond TG/DTA. EDX analysis was carried out using JEOL Model JED-2300 and the amount of metal in catalyst was determined by ICP-AES analysis using ARCOS from M/s. Spectro, Germany. CHN analysis was recorded on Thermo Finnigan FLASH EA 1112 series. SEM images were recorded using JEOL Model JSM-6390LV Scanning Electron Microscope

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and High Resolution Transmission Electron Micrographs (HR-TEM) were recorded work in the contract of the contr

Catalyst preparation

Synthesis of SiO₂-TiO₂ support [STS]

Activated SiO_2^{38} (1.0 g) was dispersed into a mixture of ethanol (40 mL) and ammonium hydroxide (5 mL) and ultrasonicated for 30 min. The solution was then transferred into a round bottom flask (100 mL) and heated at 45 °C under continuous stirring. The solution of tetrabutyl orthotitanate (TBOT, 4 mL) in ethanol (30 mL) was added into the suspension dropwise at a rate of 3 mL min⁻¹, and stirring was continued to proceed at 45 °C for 24 h. The resultant SiO₂-TiO₂ composite was filtered, washed with distilled water (3×10 mL) and ethanol (3×10 mL), and dried in an oven at 60 °C overnight.

Synthesis of amine-functionalized SiO₂-TiO₂ support [DA-STS]

To a mixture of SiO₂-TiO₂ composite (1g) and ethane-1,2-diamine (0.3 g, 5 mmol) [or butane-1,4-diamine (0.44 g, 5 mmol) or hexane-1,6-diamine (0.68 g, 5 mmol)] in a round bottom flask (50 mL), deionized water (10 mL) was added and the reaction mixture was stirred at 120 °C for 8 h. Diamine functionalized SiO₂-TiO₂ support [12DA-STS prepared from ethane-1,2-diamine; 14DA-STS prepared from butane-1,4-diamine; 16DA-STS prepared from hexane-1,6-diamine] was filtered, washed with water (3×10 mL) and ethanol (3×10 mL), and dried under vacuum at room temperature to get light grey powder.

Synthesis of palladium-copper (1:1) onto amine functionalized SiO_2 -Ti O_2 support [Pd₁Cu₁@12DA-STS, Pd₁Cu₁@14DA-STS and Pd₁Cu₁@16DA-STS]

To a solution of $Pd(OAc)_2$ (0.023g, 0.1 mmol) in ethanol (10 mL), $Cu(OAc)_2$ (0.020g, 0.1 mmol) in ethanol (10 mL) was added and stirred for 2 h. To this solution, ethane-1,2-diamine functionalized SiO₂-TiO₂ support (1.0 g) was added and the reaction mixture was stirred at room temperature for another 3 h. Finally, freshly prepared aqueous solution of NaBH₄ (1.5 mmol, 5 mL) was added dropwise over a period of 3 h followed by further stirring for 8 h at room temperature. The reaction mixture was then filtered and the catalyst was successfully washed with distilled water (3×10 mL) and ethanol (3×10 mL) respectively. The prepared grey coloured Pd₁Cu₁@12DA-STS was dried in vacuum at room temperature overnight.

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Similarly, $Pd_1Cu_1@14DA$ -STS and $Pd_1Cu_1@16DA$ -STS were prepared by similar procedure using 14DA-STS and 16DA-STS respectively.

Synthesis of palladium-copper [1:3 and 3:1] onto ethane-1,2-diamine functionalized SiO₂-TiO support [Pd₁Cu₃@12DA-STS] and Pd₃Cu₁@12DA-STS]

To a solution of $Pd(OAc)_2$ (0.0112g, 0.05 mmol) in ethanol (10 mL), $Cu(OAc)_2$ (0.030g, 0.15 mmol) in ethanol (10 mL) was added in case of $Pd_1Cu_3@12DA-STS$ and [or $Pd(OAc)_2$ (0.0337g, 0.15 mmol) and $Cu(OAc)_2$ (0.010g, 0.05 mmol) in case of $Pd_3Cu_1@12DA-STS$] and the resulting mixture was stirred for 2 h. To this solution, ethane-1,2-diamine functionalized SiO_2 -TiO₂ support (1 g) was added and the reaction mixture was stirred at room temperature for another 3 h. Finally, freshly prepared aqueous solution of NaBH₄ (1.5 mmol, 5 mL) was added dropwise over a period of 3 h followed by further stirring for 8 h at room temperature. The reaction mixture was then filtered and the catalyst was successfully washed with distilled water (3×10 mL) and ethanol (3×10 mL) respectively. The prepared catalysts $Pd_1Cu_3@12DA-STS$ and $Pd_3Cu_1@12DA-STS$ were dried in vacuum at room temperature overnight.

Similarly, monometallic Pd(0)@)12DA-STS and Cu(0)@)12DA-STS were also prepared by using 0.1 mmole of $Pd(OAc)_2$ and $Cu(OAc)_2$ seperately following the same procedure.

Catalytic test

General procedure for Pd₁Cu₁@12DA-STS catalyzed Chan-Lam cross-coupling of aromatic amines with phenylboronic acid

Aryl amine (1 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (1.2 mmol) and $Pd_1Cu_1@12DA$ -STS (0.1g) were dispersed in water:ethanol (3:1, 8 mL) and the reaction mixture was stirred at 70 °C for the appropriate time. After completion of the reaction (monitored by TLC), the catalyst was filtered, washed with ethyl acetate (3×5 mL) followed by deionized water (2×10 mL) and dried under vacuum. The reaction mixture was cooled and extracted with ethyl acetate (20 mL). The organic layer was washed with deionized water (3×20 mL) and dried over anhydrous Na₂SO₄. The product was obtained after passing through column of silica gel and elution with EtOAc-pet. ether.

General procedure for Pd₁Cu₁@12DA-STS catalyzed Suzuki coupling of aryl halides With ticle Online phenylboronic acid

To a mixture of aryl halide (1 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (0.25 mmol) and Pd₁Cu₁@12DA-STS (0.1 g) in a round bottom flask (25 mL), water:ethanol (3:1, 8 mL) was added and the reaction mixture was stirred for the appropriate time at 70 °C. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with ethyl acetate (10 mL) and filtered. The organic layer was washed with water (50 mL) and dried over anhydrous Na₂SO₄. Finally, the product was obtained by column chromatography on silica gel (EtOAc:pet.ether). The catalyst was washed with EtOAc (3×5 mL) and double distilled water (3×10 mL) and dried under vaccum overnight at room temperature for further use. The structures of the products were confirmed by ¹H and ¹³C NMR spectral data.



Scheme 1. General procedure for the synthesis of $Pd_1Cu_1@12DA-STS$.

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3. Results and discussion

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Characterization of Pd₁Cu₁@12DA-STS

Bimetallic Pd₁Cu₁@12DA-STS, Pd₁Cu₁@14DA-STS and Pd₁Cu₁@16DA-STS were synthesized by changing the amine moiety. Further, monometallic Pd(0)@)12DA-STS, Cu(0)@)12DA-STS and bimetallic Pd₁Cu₃@12DA-STS and Pd₃Cu₁@12DA-STS were prepared by changing the composition of Pd and Cu (**Scheme 1**). All the catalysts were characterized by Fourier Transform Infrared Spectroscopy (FT-IR) and Thermogravimetric Analysis (TGA). While the most active heterogeneous catalyst was further characterized by Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (HR-TEM), Carbon, Hydrogen and Nitrogen (CHN) analysis, BET (Brunauer-Emmett-Teller) analysis, Energy Dispersive X-ray analysis (EDX), Inductively Coupled Plasma Atomic Emission Spectroscopy (XPS).

The FT-IR spectral analysis of the synthesized catalysts was done to study their surface chemical structure. All the catalysts i.e. Pd₁Cu₁@14DA-STS, Pd₁Cu₁@16DA-STS Pd₁Cu₁@12DA-STS, Pd₁Cu₃@12DA-STS and Pd₃Cu₁@12DA-STS showed almost similar peaks due to the presence of same functionalities in them. The FT-IR spectra of STS, 12DA-STS and Pd₁Cu₁@12DA-STS are shown in S1 and Fig. 1 respectively. The peaks at 1085, 795 and 474 cm⁻¹ are probably due to asymmetric stretching (v_{as}), symmetric stretching (v_s) and deformation modes of Si-O-Si respectively. A typical band at 943 cm⁻¹ has been assigned to the asymmetric stretching of Si-O-Ti, clearly indicating the formation of SiO₂-TiO₂ composite^{20, 24, and 39}. A broad band in the range of $3400-3100 \text{ cm}^{-1}$ can be attributed to the stretching vibrations of surface O-H and N-H groups on the surface of the material as well as adventitious water. The characteristic peaks at 2919 cm^{-1} and 1633 cm^{-1} were assigned to the stretching vibrations of the C-H stretching of the CH₂ group and the bending vibrations of the N-H of the NH₂ group respectively, signifying the presence of an ethylene diamine moiety on the catalyst. The peaks at 1085 cm⁻¹ and 1299 cm⁻¹ were attributed to C-H deformation and C-N stretching vibrations respectively. To investigate the thermal stabilities of the catalysts, a thermo-gravimetric analysis (TGA) was carried out by heating the material at a rate of $10 \circ C \text{ min}^{-1}$. The difference in thermal stabilities of all the three

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Fig. 1 FTIR of $Pd_1Cu_1@12DA$ -STS.

bimetallic catalysts may be due to the different ratios of metals thus affecting the covalent bonding between the silica-titania support and the amine moiety. TGA of Pd₁Cu₁@12DA-STS, the most active catalyst, showed an initial weight loss of 0.75% up to 160 °C which is likely to be due to the loss of adsorbed solvent or water from the catalyst. It was followed by continuous weight loss of ca. 8% upto 321°C, which could be due to the thermal decomposition of chemisorbed molecules of diamine moiety present in the catalyst. Further weight loss from 530 to 900°C was attributed to the bulk pyrolysis of silica-titania composite. The analysis indicated that the catalyst is stable upto 160°C, thus confirming that it could be safely used for carrying out the reactions under optimum conditions (upto 80°C). The major weight loss of 12DA-STS, Pd₁Cu₃@12DA-STS and Pd₃Cu₁@12DA-STS are presented in S2. The shape and surface morphology of $Pd_1Cu_1@12DA$ -STS was studied by scanning electron microscopy at different magnifications (Fig. 3). SEM images revealed that the synthesized catalyst is homogeneous in nature and Pd and Cu nanoparticles were uniformly spread over the surface of amine functionalized silica-titania support with partial surface exposure (Fig. 3b). Their spherical shape results in low tendency of nanoparticles to undergo agglomeration, thereby increasing the surface area of the catalyst and hence the observed increased catalytic efficiency.

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Fig. 2 TGA of Pd₁Cu₁@12DA-STS.



Fig. 3 SEM images (a, b) of Pd₁Cu₁@12DA-STS.

The morphology and distribution of Pd and Cu onto 1,2-diamine functionalized silica-titania support was further verified by high resolution transmission electron microscopy (Fig. 4). The high magnification HR-TEM images of Pd₁Cu₁@12DA-STS shows black coloured

spots, which could be ascribed to the presence of Pd(0) and Cu(0) nanoparticles formed Vias Adjicle Online result of the coordination of Pd and Cu with the surface of the support (**Fig. 4b**). The average size of PdCu nanoparticles was 5~7 nm as depicted by the histogram. The nanoparticles are dispersed homogeneously without any noticable aggregation onto the surface of 1,2-diamine functionalized silica-titania support.



Fig. 4 HR-TEM images (a, b) of $Pd_1Cu_1@12DA$ -STS.

The elemental composition of Pd₁Cu₁@12DA-STS was analyzed by energy dispersive spectroscopy (EDX). The EDX analysis reveals that the catalyst is composed of C, O, Si, Ti, Cu and Pd which indicate that PdCu nanoparticles were successfully incorporated over the amine functionalized silica-titania support (**Fig. 5**). CHN analysis further confirms the presence of amino group in Pd₁Cu₁@12DA-STS [**S3**]. The porous properties and the surface area estimation of the prepared catalyst was determined by nitrogen adsorption-desorption analysis^{3a} (Fig. 5). The resulting plot can be considered as a composite of type II and type IV isotherm with an H3-type hysteresis loop, which are associated to the microporous and mesoporous materials with slit like pores. The BET surface area of the Pd₁Cu₁@12DA-STS was found to be 86.335 m² g⁻¹ and a total pore volume as 0.34 cm³ g⁻¹



Fig. 5 Nitrogen adsorption-desorption isotherm of Pd₁Cu₁@12DA-STS.



Fig. 6 EDX of $Pd_1Cu_1@12DA$ -STS.

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In order to determine the content of palladium and copper loaded onto the support material Article Online the synthesised catalyst was analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results indicated that palladium and copper content loaded onto 0.1g of Pd₁Cu₁@12DA-STS was found to be 0.478 wt% and 0.972 wt% respectively. To get further insight into the structure of the catalyst, the presence of palladium and copper nanoparticles onto Pd₁Cu₁@12DA-STS was also confirmed by powder X-ray diffraction (XRD) analysis (Fig. 6). The XRD pattern of Pd₁Cu₁@12DA-STS exhibits the diffraction patterns at $2\theta = 43.4$, 50.5, and 74.2° which can be indexed as [111], [200] and [220] planes of copper. A strong diffraction peak at 42.4° along with a weak peak at 49.5° was observed between the diffraction peaks from (111) and (200) facets of monometallic Pd and Cu, which indicates the formation of PdCu nanoalloy^{40, 41}. Fairly broad peaks were observed around 41°, 46.7° and 68.1° which are related to Pd-Cu alloy in the fcc phase. Diffraction peaks at 25.2, 48.1 and 53.8° correspond to the [101], [200] and [105] planes of the cubic phase of TiO₂, while the peak at 22° is assigned to crystalline silica. The average particle size of the catalyst, determined using Scherrer equation (5.931 nm) was found to be in close agreement with the particle size obtained from HR-TEM studies.



Fig.7 XRD of Pd₁Cu₁@12DA-STS.

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X-ray photoelectron spectroscopy (XPS) was employed to further understand the surface fride Online Online



Fig. 8 XPS of $Pd_1Cu_1@12DA$ -STS.

The peaks corresponding to carbon 1s (284.8 eV), oxygen 1s (532.3 eV), nitrogen 1s (401.4 eV), silica 2p (105.3 eV), titanium 2p (456.02-459.8 eV), palladium 3d (336.7 eV) and copper 3d (932.9 eV) are clearly observed. **Fig.7b** shows the typical Pd(0) absorptions at 336.7 and 339.2 eV for 3d5/2 and 3d3/2 respectively which is slightly shifted to higher binding energies as compared to the monometallic Pd $3d5/2^{41-43}$. While comparing the XPS

of Cu 2p3/2 for monometallic Cu⁴⁴ to those obtained for the bimetallic catalies article online (Pd1Cu1@12DA-STS), a progressive shift to lower binding energy was observed. **Fig. 7c** shows the typical Cu(0) absorptions at 932.1 and 952.5 eV, attributed to the binding energy of Cu 2p3/2 and Cu 2p5/2 respectively⁴⁵, which may be related to Cu-M, where M can be either Pd or Cu.

Catalyst testing for C-N bond formation

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59 60 The catalytic performance of the synthesized bimetallic catalysts and their monometallic analogues was studied in C-N bond forming reactions. We investigated the effect of pendent chain length by changing the amine moiety in order to find the most active catalyst among the supported PdCu bimetallic catalysts studied (Table 1). We selected the reaction of 4methoxyaniline and phenylboronic acid as the model reaction. It was found that shortest carbon chain length on the support provided the best results compared to other amine moieties (Table 1, entries 6, 9, 12). This may be due to the trapping of metal nanoparticles more efficiently by the basic nitrogen sites of ethane-1,2-diamine present on the support material. We also examined the influence of the metal composition on the reaction efficiency. The model reaction was carried out using supported PdCu catalysts with different composition of Pd and Cu. It was found that catalysts with pure copper or mainly copper gave lower product yields (Table 1, entry 9 and 16). In contrast, catalysts consisting predominently of palladium (Table 1, entry 6 and 15) showed better results. The catalytic system containing equal amounts of Pd and Cu showed higher activity (Table 1, entry 12) as compared to the other metal compositions (Table 1, entries 13-16) and their monometallic counterparts. During our studies on exploring the catalytic performance of Pd₁Cu₁@12DA-STS for C-N cross-coupling reaction, various reaction parameters such as, reaction temperature, catalyst screening, the presence of base and the effect of solvents were investigated. Initially, the model reaction was performed using 0.1g of different supported monometallic and bimetallic catalysts for optimization of the appropriate catalyst amount, while other conditions remained the same. The results are summarized in Table 1. When the model reaction was attempted with only 0.05g of the same catalyst, it led to a slight decrease in product yield (Table 1, entry 17). The effect of solvent was studied by carrying out the model reaction in different solvents, including water, acetonitrile, toluene, ethanol, methanol, H₂O/EtOH (3:1), H₂O/EtOH (1:1) and H₂O/EtOH (1:3). The results are summarized in Table 2. With water, acetonitrile, toluene and methanol, the reaction did not

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progress to completion even with longer reaction times (Table 2, entries 1-5 and 7) But Article Online we got good results when ethanol was used as a solvent. The model reaction was also carried out in ethanol:water mixtures in different ratios and we found that H₂O/EtOH (3:1) was superior in terms of both the yield and the reaction time (Table 2, entry 10). In order to study the importance of the base, the model reaction was tested in the absence of base giving only 25-40% of product (Table 2, entries 1, 9, 13, 15). When the reaction was performed in the presence of K_2CO_3 as base, the reaction gave more satisfactory results at 70 °C (Table 2, entry 10). After optimization of the reaction conditions, the generality of the developed protocol was studied with respect to different aromatic amines and overall good results were obtained (Table 3). Further, the reaction was also carried out using aliphatic amines but only trace amounts of products were obtained that too after long reaction times, except for butyl amine which showed good results (Table 3, entry 2m). The reaction proceeds faster with better yield in the case of 4-methoxyaniline (Table 3, entry 2b) as compared to 2methoxyaniline (Table 3, entry 2c). With 4-fluoroaniline (Table 3, entry 2f) and 2fluoroaniline (Table 3, entry 2j), the coupling products were obtained in good yields, whereas in the reaction of 4-bromoaniline with phenyl boronic acid (Table 3, entry 2g), we witnessed the formation of a side product (C-C coupling product, Table 3, entry 2h) though only in small amount along with the C-N coupling product. Similar results were obtained for 4-chlorophenylboronic acid (Table 3, entry 2r), wherein C-C coupling product 2s was also formed as the side product. Reaction with 2-iodoaniline (Table 3, entry 2k) led to significant decrease in C-N product formation because of the good leaving nature of the iodo group. Instead it formed C-C coupling product (Table 3, entry 21) as the major product. Low yield was obtained in case of diphenylamine (Table 3, entry 20) and diethylamine (Table 3, entry 2t) with longer reaction time, whereas, imidazole and indoles did not form the expected coupling products. Further, 2-thiomethylphenylboronic acid fails to couple with 4-methoxyaniline, which may be due to the presence of sulphur in the substrate. Only trace amount of expected product was detected with 2-thiopheneboronic acid, which could not be isolated.

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Table 1. Optimization of the catalyst amount for C-N cross-coupling reaction, <u>comparison</u> of the catalytic activity of various supported monometallic and bimetallic catalysts, and effect of metal composition on reaction efficiency^a

Entry	Catalyst	Amount (g)	Time (h)	Yield ^b (%)
	No catalyst	<u>0 1</u> σ	8	NR
2	STS	0.1g	8	Traces
3	Pd@STS	0.1	6	45
4	Cu@STS	0.1	6	50
5	PdCu@STS	0.1	6	58
6	Pd@12DA-STS	0.1	6	72
7	Pd@14DA-STS	0.1	6	60
8	Pd@16DA-STS	0.1	5.5	64
9	Cu@12 DA-STS	0.1	5.5	70
10	Cu@14DA-STS	0.1	6	65
11	Cu@16DA-STS	0.1	6	68
12	Pd ₁ Cu ₁ @12DA-STS	0.1	2.5	90
13	Pd ₁ Cu ₁ @14 DA-STS	0.1	5.5	80
14	Pd ₁ Cu ₁ @16 DA-STS	0.1	5.5	74
15	$Pd_3Cu_1@12 DA-STS$	0.1	5.5	74
16	Pd ₁ Cu ₃ @12 DA-STS	0.1	4.0	72
17	Pd ₁ Cu ₁ @12 DA-STS	0.05	4.5	86

^aReaction conditions: 4-methoxybenzenamine (1 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (1.2 mmol, 0.165 g) in $H_2O/EtOH$ (3:1, 8 mL) at 70 °C; ^bChromatographic yield.

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58 59 60 **Table 2.** Effect of various reaction parameters for C–N and C–C couplings in the presence of Pd₁Cu₁@12DA-STS

S.No.	Solvent	Base	Temperature	C-N	Coupling ^a	C-C	Coupling ^b
			(°C)	Time	Yield ^c	Time	Yield ^c
				(h)	(%)	(h)	(%)
1	Water	-	RT	8.0	25	3.5	42
2	Water	K ₂ CO ₃	RT	8.0	25	3.5	52
3	Water	K ₂ CO ₃	100	6.0	65	3.0	82
4	Acetonitrile	K ₂ CO ₃	RT	6.5	35	2.5	70
5	Toluene	K ₂ CO ₃	RT	6.0	35	3.0	60
6	Ethanol	K ₂ CO ₃	70	5.5	65	3.0	78
7	Methanol	K ₂ CO ₃	RT	6.0	35	3.5	74
8	H ₂ O/EtOH (3:1)	K ₂ CO ₃	RT	6.0	55	2.0	80
9	H ₂ O/EtOH (3:1)	-	70	6.0	35	2.5	54
10	H ₂ O/EtOH (3:1)	K ₂ CO ₃	70	2.5	90	0.25	88
11	H ₂ O/EtOH (1:1)	K ₂ CO ₃	RT	6.0	55	2.0	78
12	H ₂ O/EtOH (1:1)	K ₂ CO ₃	70	4.0	82	0.5	88
13	H ₂ O/EtOH (1:1)	-	70	5.5	40	2.5	52
14	H ₂ O/EtOH (1:3)	K ₂ CO ₃	RT	6.0	40	1.75	84
15	H ₂ O/EtOH (1:3)	-	70	6.0	35	3.0	48
16	H ₂ O/EtOH (1:3)	K ₂ CO ₃	70	4.5	86	0.75	86

^aReaction conditions: 4-methoxybenzenamine (1 mmol), phenylboronic acid (1.2 mmol), K₂CO₃ (1.2 mmol, 0.165 g), Pd₁Cu₁@12DA-STS (0.1 g , 0.75 mol% Cu, 0.91 mol% Pd). ^bReaction conditions: bromobenzene (1 mmol), phenyl boronic acid (1.2 mmol), K₂CO₃ (0.25 mmol, 0.165 g), Pd₁Cu₁@12DA-STS (0.1 g, 0.75 mol% Cu, 0.91 mol% Pd). ^cChromatographic yield.

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^aReaction conditions: aryl amine (1 mmol), arylboronic acid (1.2 mmol) $Pd_1Cu_1@12DA-STS$ (0.1 g, 0.75 mol% Cu, 0.91 mol% Pd.), K_2CO_3 (1.2 mmol, 0.165 g) in $H_2O/EtOH$ (3:1, 8 mL) at 70 °C; ^bChromatographic yield.; 2h, 2l, 2s: C-C coupling takes place along with C-N cross-coupling.

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Encouraged by the catalytic proficiency of our new designed bimetallic catalyst, Pd₁Cu₁@12DA-STS for C-N bond formation, its catalytic activity was further explored in Suzuki couplings. The reaction parameters such as catalyst amount, temperature and solvent were optimized based on the reaction of bromobenzene and phenylboronic acid as a test reaction. The optimum conditions were found to be: bromobenzene (1 mmol), phenylboronic acid (1.2 mmol), Pd₁Cu₁@12DA-STS (0.1 g, 0.75 mol% Cu, 0.91 mol% Pd), H₂O/EtOH (3:1) as solvent, 70 °C and with K₂CO₃ as the base. Suzuki coupling also occurs in the presence of a base but since the synthesised catalyst, Pd₁Cu₁@12DA-STS is base functionalized, the test reaction was attempted in the absence of base. We did not get very good results and the corresponding products were obtained in only 42-54% yield (Table 2, entries 1, 9, 13, 15). The test reaction was tried with only 0.25 mmole of K₂CO₃ which did give good results. These results supported the observation that the base functionalised catalyst requires a limited amount of base - about eight times lower than the reported Suzuki coupling reaction⁴⁶. In order to evaluate the generality of the developed method, the C-C coupling reaction was extended to different aryl halides and phenylboronic acids, substituted with both electron-donating and electron-withdrawing groups. The reaction proceeded smoothly to give the products in quantitative yields (Table 4). The reaction with indole also worked well but lower yields were obtained as compared to aryl halides (Table 4, entry 3j-I). It is pertinent to mention that exclusively C-C coupling take place and there is no evidence for the C-N coupling reaction under the selected conditions.

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 $Pd_{I}Cu_{I} @ 12 DA\text{-}STS \\$

B(OH)₂

Br



^aReaction conditions: aryl halide (1 mmol), arylboronic acid (1.2 mmol), $Pd_1Cu_1@12DA-STS$ (0.1 g, 0.75 mol% Cu, 0.91 mol% Pd), K_2CO_3 (0.25 mmol, 0.0345 g) in $H_2O/EtOH$ (3:1, 8 mL) at 70 °C; ^bChromatographic yield.

Recyclability

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The recovery of the catalyst is most crucial in order to save energy, time and resources for sustainable organic synthesis. The reusability of $Pd_1Cu_1@12DA$ -STS catalytic system was checked in case of entry 2b, Table 3 and entry 3g, Table 4 under the selected conditions. After completion of the reaction, the catalyst was easily separated by simple filtration, washed with ethyl acetate and distilled water, dried and used in the next cycle. The activity of the catalyst was investigated for five consecutive runs and the results are presented in Table 5. These clearly indicate that the catalyst is recyclable upto five runs without any significant loss of catalytic activity.

	<u>C-N coupling</u>	2 ^a	C-C Coupling ^b		
Catalytic runs	Catalyst amount (g)	Yield (%) ^c	Catalyst amount (g)	Yield (%) ^c	
1	0.1	90	0.1	88	
2	0.092	88	0.094	88	
3	0.088	86	0.090	87	
4	0.082	84	0.086	84	
5	0.076	78	0.081	81	

Table 5. Recyclability of Pd₁Cu₁@12DA-STS for C-N and C-C coupling reaction

^aReaction conditions: 4-methoxybenzenamine (1 mmol), phenylboronic acid (1.2 mmol), Pd₁Cu₁@12DA-STS (0.1 g , 0.75 mol% Cu, 0.91 mol% Pd), K₂CO₃ (1.2 mmol, 0.165 g) in H₂O/EtOH (3:1, 8 mL) at 70 °C. ^bReaction conditions: bromobenzene (1 mmol), phenylboronic acid (1.2 mmol), Pd₁Cu₁@12DA-STS (0.1 g, 0.75 mol% Cu, 0.91 mol% Pd), K₂CO₃ (0.25 mmol) in H₂O/EtOH (3:1, 8 mL) at 70 °C; ^cChromatographic yield.

Conclusion

Amine functionalized SiO₂-TiO₂ supported bimetallic PdCu catalysts have been synthesised and characterized for carrying out C-N and C-C coupling reactions. Amine functionalization of SiO₂-TiO₂ support was done by ethane-1,2-diamine, butane-1,4-diamine and hexane-1,6diamine so as to study the effect of pendant chain length on stabilization of bimetallic nanoparticles. PdCu metal alloy nanoparticles immobilized onto ethane-1,2-diamine functionalized SiO₂-TiO₂ support with metal ratio of 1:1 was found to be the most active catalytic system. The remarkable synergetic effect between the two metals and the presence of basic nitrogen sites onto the support effectively stabilize and enhance the activity by preventing agglomeration. Our catalyst exhibits excellent activity under less basic conditions, than normal and with excellent yields for the C–C coupling reaction. Moreover Article Online the developed catalyst ensures easy recovery and reusability upto five consecutive runs.

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Appendix A. Supplementary data

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Diamines as interparticle linkers for silica-titania supported PdCu bimetallic nanoparticles in Chan-Lam and Suzuki cross-coupling reactions

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The remarkable synergetic effect between Pd and Cu, and basic nitrogen sites onto the support effectively stabilize the nanoparticles and enhance the catalytic activity.

