

Magnetic Nanoparticle-Supported N-Heterocyclic Carbene-Palladium(II): A Convenient, Efficient and Recyclable Catalyst for Suzuki–Miyaura Cross-Coupling Reactions

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Abstract A new magnetic nanoparticle-supported N-heterocyclic carbene-palladium(II) nanomagnetic catalyst was synthesized and appropriately characterized using attenuated total reflectance infrared spectroscopy (ATR-IR), ultraviolet–visible spectroscopy (UV–Visible), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), energy-dispersive X-ray spectroscopy (EDS), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), thermogravimetric analysis (TGA) and Brunauer– Emmett–Teller surface area analysis (BET). The nanomagnetic catalyst was used as convenient and efficient catalyst for the Suzuki–Miyaura cross-coupling reaction of various aryl bromides/chlorides/iodide with phenylboronic acid. The effects of varying solvents, bases, temperature, time and catalytic ratios on the performance of the Suzuki– Miyaura cross-coupling reaction were investigated. The notable advantages of this heterogeneous nanomagnetic catalyst are excellent yields, mild reaction conditions, short reaction times and easy work-up. Moreover, the new nanomagnetic catalyst could be easily recovered with an external magnet and could be reused at least five times without loss of its catalytic activity.

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1 Introduction

A catalyst plays an important role in chemical transformations by decreasing the time of reaction, increasing the conversion of starting materials to products thereby increasing the yield and reducing waste generation [1]. Two types of catalysts, homogeneous and heterogeneous, are classified based on their physical state in a chemical reaction. Both homogenous and heterogeneous catalysts have their own advantages and disadvantages [2, 3]. An advantage of homogenous catalysts is their placement in the same phase as that of reactants; hence, they are more efficient and the rate of reaction will be high [4]. But for this same reason, it is difficult to separate homogeneous catalysts from products, lowering their recovery after completion of the reaction. In the case of heterogeneous catalysts, they will not be present in same phase as that of reactants. As a result, the efficiency will be less and reaction rate will not be as high as that using homogenous catalysts [5]. However, a distinct advantage of heterogeneous catalysts is their easy isolation after reaction completion. Therefore, there is a need for a catalyst which can increase the efficiency of the reaction (homogenous-like) and can be isolated easily after reaction completion (heterogeneous-like).

In 1991, Arduengo isolated N-heterocyclic carbene (NHC) as the first free, stable carbene through deprotonation of 1,3-bisadamantyl imidazolium chloride [6]. Later, in 1995, Herrmann and co-workers reported the first use of NHC ligands in catalytic applications [7]. After that, NHC ligands have attracted much attention as appropriate transition metal ligands. Recently, NHCs have drawn much attention as substitutes for phosphines because of higher dissociation energies, less toxicity, stability in air and moisture, analogous σ -donor and low σ -acceptor abilities, and the formation of stronger bonds with various transition metals [8–18]. On the other hand, NHC-metal complexes show high thermal stabilities, and the electronic and steric properties of NHCs may be tuned, which is an added advantage for the development of novel organometallic materials [19]. Consequently, NHC-metal complexes have been used extensively as convenient and efficient homogeneous catalysts in numerous organic transformations, such as carbon–carbon (C–C) and carbon–nitrogen (C–N) cross-coupling reactions [20–35]. NHC-palladium(II) complexes have shown very good catalytic activity in the Suzuki–Miyaura cross-coupling reactions, which have many applications in the preparation of natural products, fine chemicals and various intermediates for drugs [36, 37].

Recently, various types of NHC-palladium(II) complexes have been developed as heterogeneous catalysts for C-C bond formation reactions through immobilizing palladium(II) on various solid supports [38–42]. But these heterogeneous catalysts suffer from many difficulties such as easy agglomeration, and leaching of palladium(II) from the catalyst to the reaction mixture. Hence, the design and synthesis of new catalysts that are not only active and stable, but also easy to separate and reuse, is extremely necessary to facilitate the C-C bond formation reactions. When nanoparticles are employed as a catalytic support, it has the advantage of being inert in most chemical environments, allowing the immobilized catalyst to behave as it would in its free state. But the separation of these nanoparticles requires techniques like nanofiltration, centrifugation, or precipitation-flocculation [43]. To overcome these difficulties, magnetite and other superparamagnetic nanoparticles are employed as a catalyst support, which possess the advantage of high surface area and easy recovery and recycling of catalyst. In this regard, magnetic separation offers a convenient and efficient method for C-C crosscoupling reactions [44]. Also, the synthesis and characterization of NHC-palladium(II) complexes on the surface of magnetic nanoparticles, with high catalytic activity in Suzuki-Miyaura cross-coupling reactions, are rare and only few examples have been reported thus far [45-47].

Since NHCs are stabilized by bulky substituents on the nitrogen atoms, we have selected benzyl bromide for substitution on one nitrogen and 3-chloropropyltriethoxysilane on the other nitrogen. Also, the strong affinity of magnetite towards silica makes silanes very useful for the functionalization of magnetite [43]. Herein, we present the synthesis and characterization of a new magnetic nanoparticlesupported NHC-palladium(II) nanomagnetic catalyst for Suzuki-Miyaura cross-coupling reactions of various aryl bromides/chlorides/iodide with phenylboronic acid. The nanomagnetic catalyst is air- and water-stable, and can be synthesized in high yield with high purity from inexpensive commercially available starting materials. Furthermore, this catalyst is shown to exhibit high catalytic activity in Suzuki-Miyaura cross-coupling reactions. In addition, the nanomagnetic catalyst may be easily isolated from the reaction medium by using an external magnet, and can then be reused in the next reaction cycle without significant loss of activity.

2 Experimental

2.1 Materials

Unless otherwise stated, all reactions were performed under aerobic conditions in oven-dried glassware with magnetic stirring. FeCl₃·6H₂O, FeCl₂·4H₂O, sodium carbonate, potassium hydroxide, ammonium hydroxide, benzyl chloride, benzimidazole, 3-chloropropyl triethoxysilane, palladium acetate, aryl halides and phenylboronic acid were purchased from Sigma-Aldrich chemical company and were used without further purification. Solvents were dried and degassed using a JC Meyer company solvent purification system. Heating was accomplished by either a heating mantle or silicone oil bath. Reactions were monitored by thin-layer chromatography (TLC) performed on 0.25 mm Merck TLC silica gel plates, using UV light as a visualizing agent. Purification of reaction products was carried out by flash column chromatography using silica gel 60 (230-400 mesh). Yields refer to chromatographically pure material. Concentration in vacuo refers to the removal of volatile solvent using a rotary evaporator attached to a dry diaphragm pump (10-15 mm Hg), followed by pumping to a constant weight with an oil pump (<300 mTorr).

2.2 Characterization

Attenuated total reflectance infrared spectra were recorded with Bruker Alpha Eco-ATR spectrometer. UV-visible spectrophotometry was carried out using a SHIMADZU UV-1800 A11454907691 spectrophotometer. Brunauer-Emmett-Teller surface areas were obtained by physisorption of N2 using Microtrac BELSORP MAX instrument. The elemental palladium content of the nanomagnetic catalyst was determined using a Thermo Electron IRIS INTREPID II XSP DUO inductively coupled plasma-atomic emission spectrophotometer. Transmission electron microscope images were obtained using Jeol/JEM 2100 microscope. FESEM images along with energy-dispersive X-ray spectroscopy to observe morphology and elemental distributions respectively were obtained using a JEOL Model-JSM7100F microscope. Thermogravimetric analysis was carried out using a Perkin-Elmer Diamond TG/DTA, with a heating rate of 10.0 °C/min. Powder X-ray diffraction was carried out using a Bruker AXS D8 Advance diffractometer. ¹H NMR spectra were recorded at 400 MHz, and are reported relative to CDCl₃ (67.27). ¹H NMR coupling constants (J) are reported in Hertz (Hz) and multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet),

m (multiplet). Liquid chromatography mass spectra (LC-MS) were recorded on Agilent technologies quadrupole LC-MS system. Elemental analyses of compounds were done on Euro Vector S.P.A, Euro EA 3000 CHNS elemental analyzer.

2.3 Synthesis of Hydroxyl Substituted Magnetic Nanoparticles (Fe₃O₄)

The hydroxyl-substituted magnetic nanoparticles (MNPs) were synthesized through a chemical co-precipitation method. A mixture of FeCl₃·6H₂O (2.35 g, 8.7 mmol) and FeCl₂·4H₂O (0.86 g, 4.3 mmol) were dissolved in deionized water (40 mL). The resultant solution was stirred for 30 min at 85 °C to completely dissolve both the reactants. Then, an ammonium hydroxide (5 mL) solution was added slowly with vigorous stirring at 85 °C to produce a black solid. The reaction was continued for an additional 30 min. The black-colored magnetic nanoparticles were isolated by magnetic decantation, washed repeatedly with deionized water until neutrality, and further washed with ethanol (2 × 20 mL) and dried at 80 °C for 6 h.

2.4 Synthesisof Silyl Chloride Functionalized Magnetic Nanoparticles (SMNPs)

Hydroxyl-substituted magnetic nanoparticles (2.0 g) were suspended in an ethanol (EtOH):water (H₂O) (1:1) mixture (20 mL) by ultrasonicating for 30 min. 3-chloropropyl triethoxysilane (2.0 g, 8.3 mmol) was added to the suspension and stirred at 45 °C for 24 h. Then, the solution was cooled to room temperature. The resultant dark brown silyl chloride functionalized magnetic nanoparticles were isolated by magnetic decantation, washed with deionized water (2×20 mL) followed by ethanol (2×20 mL) and dried at 80 °C for 6 h.

2.5 Synthesis of 1-Benzyl-1H-benzimidazole

Benzimidazole (1.0 g, 8.46 mmol) and potassium hydroxide (0.71 g, 12.69 mmol) were stirred for 2 h in a minimum amount of dimethyl sulfoxide (DMSO) at 100 °C. The temperature of the reaction mixture was reduced to 40 °C and benzyl bromide (1.45 g, 8.46 mmol) was added in one portion and stirring was continued for an additional 2 h. Afterwards, the reaction mixture was cooled to room temperature and ice cold water (20 mL) was added. The off-white solid was separated by filtration, washed with water and dried at 50 °C under vacuum to get 1-benzyl-1H-benzimidazole as an off-white solid. Yield: 97%. ¹H NMR (400 MHz, CDCl₃): δ (ppm)=7.95 (s, 1H, NCHN), 7.82 (d, *J*=6.8 Hz, 1H, NC₆H₄N), 7.34–7.18 (m, 8H, NC₆H₄N and CH₂C₆H₅), 5.36 (s, 2H, CH₂C₆H₅). Mass data (*m*/*z*, LC-MS): 209.04 $[M+H]^+$. Anal. Calc'd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45%. Found: C, 80.71; H, 5.83; N.13.47%.

2.6 Synthesis of Magnetic Nanoparticle Tethered 1-Benzyl-1*H*-benzimidazolium chloride (NHC@ MNPs)

Silyl chloride functionalized magnetic nanoparticles (2.0 g) were suspended in toluene (40 mL) by ultrasonicating for 30 min. 1-Benzyl-1*H*-benzimidazole (1.0 g, 4.8 mmol) was added in one portion to the reaction mixture and stirred at 110 °C for 48 h. Then, the reaction mixture was cooled to room temperature. The product was isolated by magnetic decantation, washed with toluene (5×20 mL) and dried at 80 °C for 12 h to yield a brown-coloured solid.

2.7 Synthesis of Magnetic Nanoparticle-Supported N-Heterocyclic Carbene-Palladium(II) Nanomagnetic Catalyst (NHC-Pd@MNPs)

To a solution of Na₂CO₃ (0.5 M, 20 mL) in dimethylformamide (DMF) (20 mL), palladium acetate (0.22 g, 0.98 mmol) was added and the resulting mixture was stirred at room temperature for 15 min. Magnetic nanoparticles tethered with 1-benzyl-1*H*-benzimidazolium chloride (1.0 g) were added and stirring was continued at 50 °C for 16 h. Then, the reaction mixture was cooled to room temperature. The resultant compound was isolated by magnetic decantation, washed with water (2×20 mL) followed by ethanol (2×20 mL) and dried at 80 °C for 6 h to yield a blackish brown-coloured solid.

2.8 General Procedure for Suzuki–Miyaura Cross-coupling Reaction

NHC-Pd@MNPs nanomagnetic catalyst (0.15 mol% Pd), aryl halide (1.0 mmol), phenylboronic acid (1.1 mmol) and potassium carbonate (2.2 mmol) were placed in a roundbottomed flask. To the mixture, EtOH:H₂O (1:1, 5 mL) was added and stirred at 70 °C for various times. The progress of the reaction was monitored by TLC. After reaction completion, the mixture was cooled to room temperature and the NHC-Pd@MNPs nanomagnetic catalyst was separated by using an external magnet. To the filtrate, ethyl acetate (10 mL) and water (10 mL) were added. Ethyl acetate layer was separated from the water layer using a separatory funnel and dried with sodium sulphate. The dried ethyl acetate was concentrated in vacuo and the product was purified by column chromatography using *n*-hexane and ethyl acetate as eluents to afford the corresponding products in good to excellent yields. All the coupling products were known molecules and were confirmed by comparing the melting point, ¹H NMR and mass spectroscopic data with the authentic samples.

- Biphenyl (Table 7, entries 1 and 2): Colorless crystals. Melting point=68–70 °C. ¹H NMR (400 MHz, CDCl₃): δ (ppm)=7.35(t, *J*=7.6 Hz,2H), 7.42 (t, *J*=7.6 Hz, 4H), 7.6 (d, *J*=8 Hz, 4H). LC-MS for C₁₂H₁₀: *m*/*z*=155.07 [M+H]⁺.
- 4-Methylbiphenyl (Table 7, entry 3): White crystalline solid. Melting point=45–47 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm)=7.79 (d, *J*=7.6 Hz, 2H), 7.65 (s, 1H), 7.40–7.36 (m, 4H), 7.32–7.28 (m, 2H), 2.27 (s, 3H). LC-MS for C₁₃H₁₂: *m/z*=169.05 [M+H]⁺.
- 3. 4-Cyanobiphenyl (Table 7, entry 4): Off-white crystalline powder. Melting point=85-87 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm)=7.43-7.41 (m, 1H), 7.50-7.47 (m, 2H), 7.58 (d, *J*=8 Hz, 2H), 7.66-7.73 (m, 4H). LC-MS for C₁₃H₉N: *m/z*=180.01 [M+H]⁺.
- 4. *4-Aminobiphenyl* (Table 7, entry 5): Purple crystals. Melting point = 52-55 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm)=7.54 (d, J=8.4 Hz, 2H), 7.41–7.38 (m, 4H), 7.29–7.24 (m, 1H), 6.76 (d, J=8 Hz, 2H), 3.75 (s, 2H). LC-MS for C₁₂H₁₁N: m/z=170.03 [M+H]⁺.
- 5. 4-Phenylbenzaldehyde (Table 7, entry 6): Yellow crystals. Melting point=57–59 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm)=10.07 (s, 1H), 7.52– 7.46 (m, 3H), 7.62 (d, J=8.4 Hz, 2H), 7.75 (d, J=6.8 Hz, 2H), 7.94 (d, J=6.8 Hz, 2H). LC-MS for C₁₃H₁₀O: m/z=183.09 [M+H]⁺.
- 6. 2-Phenylbenzaldehyde (Table 7, entries 7 and 8): Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ (ppm)=9.78 (s, 1H),7.30–7.26 (m, 3H), 7.39–7.36 (m, 2H), 7.51 (d, *J*=7.6 Hz, 1H), 7.65–7.71 (m, 2H). LC-MS for C₁₃H₁₀O: *m/z*=183.05 [M+H]⁺.
- 7. 4-Nitrobiphenyl (Table 7, entry 9): Pale yellow crystals. Melting point = 112–114 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.51–7.45 (m, 3H), 7.62 (d, J = 8.8 Hz, 2H), 7.73 (d, J = 8.8 Hz, 2H), 8.29 (d, J = 8.8 Hz, 2H). LC-MS for C₁₂H₉NO₂: m/z = 200.04 [M+H]⁺.
- 8. 4-Methoxybiphenyl (Table 7, entries 10 and 11): White powder. Melting point=86–90 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm)=7.56–7.52 (m, 4H), 7.41 (t, *J*=7.2 Hz, 2H), 7.31 (t, *J*=7.6 Hz, 1H), 6.98 (d, *J*=8.8 Hz, 2H), 3.85 (s, 3H). LC-MS for C₁₃H₁₂O: m/z=185.10 [M+H]⁺.
- 9. 4-Hydroxybiphenyl (Table 7, entries 12 and 13): White crystals. Melting point=164–166 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm)=7.53 (d, J=7.2 Hz, 2H), 7.48 (d, J=7.2 Hz, 2H), 7.39 (d, J=8.8 Hz, 2H), 7.31–7.28 (m, 1H), 6.90 (d, J=8.4 Hz, 2H), 4.8 (s, 1H). LC-MS for C₁₂H₁₀O: m/z=171.15 [M+H]⁺.

- 4-Acetylbiphenyl (Table 7, entries 14 and 15): White powder. Melting point=119–123 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm)=8.02 (d, J=8.4 Hz, 2H), 7.68 (d, J=8.8 Hz, 2H), 7.62 (d, J=7.6 Hz, 2H), 7.44–7.46 (m, 2H), 7.38–7.39 (m, 1H), 2.63 (s, 3 H). LC-MS for C₁₄H₁₂O: m/z=197.17 [M+H]⁺.
- 11. 3-Phenylbenzoic acid (Table 7, entries 16 and 17): Off-white crystals. Melting point=164–168 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm)=7.39–7.36 (m, 2H), 7.49–7.41(m, 1H), 7.64 (d, *J*=7.2 Hz, 3H), 7.74 (d, *J*=7.6 Hz, 2H), 7.84 (d, *J*=7.2 Hz, 1H). LC-MS for C₁₃H₁₀O₂: *m*/z=199.06 [M+H]⁺.
- 12. *4-Phenylbenzoic acid* (Table 7, entry 18): White solid. Melting point = 219–224 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.39–7.37 (m, 4H), 7.44–7.40 (m, 1H), 7.52–7.49 (m, 3H), 7.65 (d, *J* = 7.2 Hz, 1H). LC-MS for C₁₃H₁₀O₂: *m/z*=199.11 [M+H]⁺.
- 13. 2,4-Difluoro-1,1'-biphenyl (Table 7, entry 19): Pale yellow crystals. Melting point=61-65 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm)=7.42-7.35 (m, 4H), 7.50-7.49 (m, 2H), 7.59 (d, *J*=7.2 Hz, 2H). LC-MS for C₁₂H₈F₂: *m*/*z*=191.02 [M+H]⁺.

2.9 Procedure for Recovery of NHC-Pd@MNPs Nanomagnetic Catalyst

NHC-Pd@MNPs nanomagnetic catalyst (0.15 mol%), aryl halide (1.0 mol%), phenylboronic acid (1.1 mol%) and potassium carbonate (2.2 mol%) were placed in a round-bottomed flask. To the reaction mixture, EtOH:H₂O (1:1, 5 mL) was added and stirred at required temperature for various times. After completion of reaction, the reaction mixture was cooled to room temperature and the NHC-Pd@MNPs nanomagnetic catalyst was separated by using an external magnet. The separated NHC-Pd@MNPs nanomagnetic catalyst was washed with water (2×10 mL) followed by ethanol (2×10 mL) and dried at 80 °C for 6 h. Then, the dried NHC-Pd@MNPs nanomagnetic catalyst was used for next round of Suzuki–Miyaura cross-coupling reactions.

3 Results and Discussion

3.1 Synthesis

In the present study, a NHC-Pd@MNPs nanomagnetic catalyst was synthesized through a multistep reaction as illustrated in Scheme 1. First, hydroxyl-substituted magnetic nanoparticles (1) were prepared by a chemical co-precipitation method, followed by the functionalization of hydroxyl-substituted magnetic nanoparticles by 3-chloropropyl triethoxysilane (2) in a EtOH: H_2O



Scheme 1 Synthetic schemes for a MNPs (1), and b the NHC-Pd@MNPs nanomagnetic catalyst (6)

mixture at 45 °C. In the next step, silyl-functionalized magnetic nanoparticles (3) were reacted with1-benzyl-1*H*-benzimidazole (4) in toluene at 110 °C for 48 h. The magnetic nanoparticles tethered with 1-benzyl-1*H*-benzimidazolium chloride (5) were then treated with palladium acetate in DMF in the presence of aqueous sodium carbonate to get the desired NHC-Pd@MNPs nanomagnetic catalyst (6).

3.2 Spectroscopic and Microscopic Characterization

Chemical structures of all the synthesized compounds were confirmed through the ATR-IR spectroscopic technique. Figure 1 demonstrates ATR-IR spectra of MNPs, SMNPs and NHC-Pd@MNPs nanomagnetic catalysts. The ATR-IR spectrum of MNPs (Fig. 1a) displays a characteristic peak of Fe–O at 585 cm⁻¹ and stretching vibrations of O-H bonds at 3393 cm⁻¹. The bands observed around 991 and 2912 cm⁻¹ are attributed to the Si-O and C-H stretching vibrations of the propyl group from 3-chloropropyl triethoxysilane apart from a Fe-O stretching vibration at 584 cm⁻¹ of SMNPs (Fig. 1 (b)), which confirms the functionalization of chloropropyltriethoxvsilane on the surface of the MNPs. The ATR-IR spectrum of NHC-Pd@MNPs nanomagnetic catalyst exhibits typical bands in the range 3250–2902 cm⁻¹attributed to aromatic C-H stretching vibrations (Fig. 1c) [48, 49]. In addition, various signals characteristic of Pd-C vibrations are observed in the spectrum (1648, 1490 and 680 cm^{-1}) (Fig. 1c), which confirms the structure of the NHC-Pd@MNPs nanomagnetic catalyst [50]. Figure 2 shows the ATR-IR spectra of the NHC-Pd@MNPs nanomagnetic catalyst and reused NHC-Pd@MNPs nanomagnetic catalyst. Even after five recycles, the NHC-Pd@ MNPs nanomagnetic catalyst composition remained the same, which is further confirmed by comparison of ATR-IR spectra of the NHC-Pd@MNPs nanomagnetic catalyst (Fig. 2c) and recycled NHC-Pd@MNPs nanomagnetic catalyst (Fig. 2d).

The UV-visible spectra of a suspension of MNPs and the NHC-Pd@MNPs nanomagnetic catalyst in methanol



Fig. 1 ATR-IR spectra of a MNPs, b SMNPs, and c the NHC-Pd@ MNPs nanomagnetic catalyst



Fig. 2 ATR-IR spectra of c the NHC-Pd@MNPs nanomagnetic catalyst and d the recycled NHC-Pd@MNPs nanomagnetic catalyst

are shown in Fig. 3. The λ_{max} observed for MNPs is 370 nm, whereas in the case of NHC-Pd@MNPs nanomagnetic catalyst, the λ_{max} observed is at 387 nm. The shift in λ_{max} from 370 nm to 387 nm can be attributed to the successful surface functionalization of MNPs [51, 52].

The surface functionalization of MNPs was further confirmed by analyzing the surface area by BET. Nitrogen adsorption-desorption curves for (a) MNPs, (b) SMNPs, and (c) the NHC-Pd@MNPs nanomagnetic catalyst are shown in Fig. 4. The NHC-Pd@MNPs nanomagnetic catalyst exhibited a type-II isotherm. The amount of N₂



Fig. 3 UV–Visible spectra of a MNPs and b the NHC-Pd@MNPs nanomagnetic catalyst



Fig. 4 Nitrogen adsorption-desorption curves for a MNPs, b SMNPs, and c the NHC-Pd@MNPs nanomagnetic catalyst

adsorbed on bare MNPs was high compared to SMNPs and the NHC-Pd@MNPs nanomagnetic catalyst. The initial surface area of bare MNPs (77.47 m^2g^{-1}) got reduced by surface functionalization with 3-chloropropyl triethoxysilane (76.60 m^2g^{-1}) and was further reduced when the NHC-Pd@MNPs nanomagnetic catalyst (56.25 m^2g^{-1}) was prepared, which is evident from data obtained from the BET [53].

The morphologies and sizes of MNPs, the NHC-Pd@ MNPs catalyst and reused NHC-Pd@MNPs nanomagnetic catalyst were investigated using TEM (Fig. 5). As shown in Fig. 5a, MNPs were spherical in nature with sizes ranging from 7 to 10 nm. After anchoring of the NHC-Pd(II) complex, the support particles are quasi-spherical in nature and the sizes were in the range of 10–15 nm (Fig. 5b). Furthermore, the magnetic core as a dark spot inside the spherical NHC-Pd@MNPs nanomagnetic catalyst can be seen from the TEM image. The morphology of the recycled NHC-Pd@MNPs nanomagnetic catalyst does not show much change after being reused up to five times (Fig. 5c) [54–56].

FESEM images of the NHC-Pd@MNPs nanomagnetic catalyst and recycled NHC-Pd@MNPs nanomagnetic catalyst are shown in Fig. 6. From the FESEM image, it is clear that the NHC-Pd@MNPs nanomagnetic catalyst was made up of uniform nanometer-sized spherical particles [57–59]. The prepared NHC-Pd@MNPs nanomagnetic catalysts are narrowly distributed and well dispersed. Also, after five recycles the morphology of the nanomagnetic catalyst was not altered, which is in good agreement with TEM images of the recycled NHC-Pd@MNPs nanomagnetic catalyst. The presence of palladium atoms in NHC-Pd@MNPs nanomagnetic catalyst was confirmed by EDS (Fig. 7). The EDS spectrum shows



(a)



Fig. 6 FESEM images of a the NHC-Pd@MNPs nanomagnetic catalyst and b the recycled NHC-Pd@MNPs nanomagnetic catalyst

characteristic signals of C, N, O, Fe, Si and Pd, which further confirms the presence of a N-heterocyclic carbene-palladium(II) complex on the surface of the MNPs [57]. In order to determine the exact quantity of Pd in theNHC-Pd@MNPs nanomagnetic catalyst, ICP-AES was carried out. ICP-AES analysis shown that 6.04% w/w of palladium is loaded on the NHC-Pd@MNPs nanomagnetic catalyst.



Fig. 7 EDS spectrum of the NHC-Pd@MNPs nanomagnetic catalyst



The XRD pattern of the NHC-Pd@MNPs nanomagnetic catalyst in comparison with MNPs was investigated (Fig. 8). The XRD pattern of MNPs (Fig. 8a) indicates a cubic spinel structure with peaks attributed to Fe₃O₄ at 20 of 30.09°, 35.59°, 43.07°, 53.43°, 57.37° and 62.90° corresponding to the reflection planes of (220), (311), (400), (422), (511), and (440). On the other hand, the NHC-Pd@ MNPs nanomagnetic catalyst showed a similar XRD pattern (Fig. 8b) as MNPs. Therefore, it is clear that even after functionalization of MNPs, the phase remained same, which is in good agreement with TEM images. Also, no characteristic peaks of Pd were observed, which shows excellent dispersion of Pd sites on the MNPs [56].

The thermal stability of the MNPs and NHC-Pd@MNPs nanomagnetic catalyst was evaluated using thermogravimetric analysis, carried out under a nitrogen atmosphere between 40 and 730 °C at a rate of 10 °C min⁻¹ (Fig. 9). The thermogram of magnetic nanoparticles (Fig. 9a) showed weight loss of 6% in the range 80-200 °C corresponding to the loss of surface hydroxyl groups and moisture. The NHC-Pd@MNPs nanomagnetic catalyst (Fig. 9b) decomposes in two stages. The first step, 80–110 °C, results in a mass loss of 3% corresponding to the loss of adsorbed water molecules. In the second step, the complete loss of covalently attached organic moiety was observed in the range 110–500 °C with mass loss of 9%. Thus, on the basis of these results, grafting of the NHC onto the MNPs is confirmed [1, 57]. Furthermore, it is clear that the NHC-Pd@ MNPs nanomagnetic catalyst could be used in reactions to a temperature of ca.110 °C without decomposition, which is an added advantage for its use in Suzuki-Miyaura crosscoupling reactions that are usually performed at elevated temperatures.



Fig. 9 TGA curves of *a* MNPs and *b* the NHC-Pd@MNPs nanomagnetic catalyst

3.3 Catalytic Properties of the NHC-Pd@MNPs Nanomagnetic Catalyst

After structural characterization of the prepared NHC-Pd@MNPs nanomagnetic catalyst through spectroscopic and microscopic techniques, its catalytic activity was studied as an active and stable magnetically separable nanomagnetic catalyst in Suzuki–Miyaura cross-coupling reactions. The reaction conditions were optimized on model Suzuki–Miyaura cross-coupling reaction between bromobenzene and phenylboronic acid, as shown in Scheme 2.

The primary requirement for green synthesis is the use of green solvents. Therefore, EtOH and H_2O were given high priority as solvents during the process optimization. The reaction conditions were optimized through a series of reactions as shown in Table 1. The preliminary results revealed that using K_2CO_3 base, EtOH: H_2O (1:1) solvent, 0.15 mol% Pd of NHC-Pd@MNPs nanomagnetic catalyst at 70 °C afforded the highest yield (Table 1, entry 8).

The performance of a palladium catalyzed Suzuki–Miyaura cross-coupling reaction is known to be governed by a number of factors such as kind of solvent, base, temperature, time, catalyst ratio, etc. Hence, the effect of different solvents, bases, temperatures, time and



Scheme 2 Suzuki–Miyaura cross-coupling reaction between bromobenzene and phenylboronic acid in the presence of NHC-Pd@ MNPs nanomagnetic catalyst

 Table 1
 Optimization of conditions for Suzuki–Miyaura cross-coupling reaction of bromobenzene with phenylboronic acid in the presence of NHC-Pd@MNPs nanomagnetic catalyst

Entry	Base	Solvent	Tem- perature (°C)	Time (h)	Yield (%) ^a
1	K ₂ CO ₃	DMF	100	6	55
2	K ₂ CO ₃	DMF:H ₂ O (1:1)	80	6	70
3	K ₂ CO ₃	H ₂ O	80	3	85
4	K ₂ CO ₃	EtOH	70	3	88
5	NaOH	EtOH	70	3	40
6	K ₂ CO ₃	EtOH:H ₂ O (9:1)	70	2	90
7	K ₂ CO ₃	EtOH:H ₂ O (8:2)	70	1	92
8	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	1	95

Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), NHC-Pd@MNPs (0.15 mol% Pd with respect to aryl halide), base (2.2 mmol) and solvent (5 mL) in air

^aIsolated yield after separation by column chromatography; average of two runs

with p magne	with phenylboronic acid in the presence of NHC-Pd@MNPs nano- magnetic catalyst with various solvents								
Entry	Base	Solvent	Tem- perature (°C)	Time (h)	Yield (%) ^a				
1	K ₂ CO ₃	DMF	70	1	50				
2	K ₂ CO ₃	H ₂ O	70	1	85				
3	K ₂ CO ₃	EtOH	70	1	80				
4	K ₂ CO ₃	MeOH	70	1	78				
5	K ₂ CO ₃	THF	70	1	55				
6	K ₂ CO ₃	Toluene	70	1	70				

Table 2 Suzuki-Miyaura cross-coupling reactions of bromobenzene

Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), NHC-Pd@MNPs (0.15 mol% Pd with respect to aryl halide), base (2.2 mmol) and solvent (5 mL) in air

56

1

1

50

92

^aIsolated yield after separation by column chromatography; average of two runs

 Table 3
 Suzuki–Miyaura cross-coupling reactions of bromobenzene

 with phenylboronic acid using NHC-Pd@MNPs nanomagnetic catalyst with various bases

Entry	Base	Solvent	Tem- perature (°C)	Time(h)	Yield (%) ^a
1	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	1	95
2	Na ₂ CO ₃	EtOH:H ₂ O (1:1)	70	1	85
3	KF	EtOH:H ₂ O (1:1)	70	1	80
4	NaOH	EtOH: $H_2O(1:1)$	70	1	40
5	KOH	EtOH:H ₂ O (1:1)	70	1	55
6	Na ₃ PO ₄	EtOH:H ₂ O (1:1)	70	1	70
7	CsCO ₃	EtOH:H ₂ O (1:1)	70	1	75

Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), NHC-Pd@MNPs (0.15 mol% Pd with respect to aryl halide), base (2.2 mmol) and solvent (5 mL) in air

^aIsolated yield after separation by column chromatography; average of two runs

catalyst ratio were studied for the model Suzuki–Miyaura cross-coupling reaction between bromobenzene and phenylboronic acid (Tables 2, 3, 4, 5, 6).

3.3.1 Effect of Solvent on Suzuki–Miyaura cross-Coupling Reaction

We studied the effect of solvents on Suzuki–Miyaura cross-coupling reactions between bromobenzene and phenylboronic acid to understand the performance of the

7

8

K₂CO₃ Acetone

K₂CO₃ EtOH : H₂O (8:2) 70

 Table 4
 Suzuki–Miyaura cross-coupling reactions of bromobenzene

 with phenylboronic acid using the NHC-Pd@MNPs nanomagnetic
 catalyst at various temperatures

Entry	Base	Solvent	Tem- perature (°C)	Time(h)	Yield (%a
1	K ₂ CO ₃	EtOH:H ₂ O (1:1)	25	1	55
2	K ₂ CO ₃	EtOH:H ₂ O (1:1)	40	1	70
3	K ₂ CO ₃	EtOH:H ₂ O (1:1)	50	1	80
4	K ₂ CO ₃	EtOH:H ₂ O (1:1)	60	1	85
5	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	1	95
6	K ₂ CO ₃	EtOH:H ₂ O (1:1)	80	1	95
7	K ₂ CO ₃	EtOH:H ₂ O (1:1)	90	1	85
8	K_2CO_3	EtOH:H ₂ O (1:1)	100	1	80

Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), NHC-Pd@MNPs (0.15 mol% Pd with respect to aryl halide), base (2.2 mmol) and solvent (5 mL) in air

^aIsolated yield after separation by column chromatography; average of two runs

 Table 5
 Suzuki–Miyaura cross-coupling reactions of bromobenzene with phenylboronic acid using NHC-Pd@MNPs nanomagnetic catalyst at various time intervals

Entry	Base	Solvent	Tem- perature (°C)	Time (h)	Yield (%) ^a
1	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	0.33	60
2	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	0.5	75
3	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	0.66	80
4	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	0.83	85
5	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	1	95
6	K_2CO_3	EtOH:H ₂ O (1:1)	70	1.5	95

Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), NHC-Pd@MNPs (0.15 mol% Pd with respect to aryl halide), base (2.2 mmol) and solvent (5 mL) in air

^aIsolated yield after separation by column chromatography; average of two runs

NHC-Pd@MNPs nanomagnetic catalyst. Suzuki–Miyaura cross-coupling reactions were carried out in different solvents like DMF, H_2O , EtOH, tetrahydrofuran (THF), toluene, acetone, methanol (MeOH) and EtOH: H_2O (8:2) solvent mixture, as shown in Table 2. The results revealed that reaction went well with polar solvents except with DMF and acetone (Table 2, entries 1 and 7). Surprisingly, the NHC-Pd@MNPs nanomagnetic catalyst showed fairly good catalytic activity with the nonpolar solvent toluene (Table 2, entry 6).

 Table 6
 Suzuki–Miyaura cross-coupling reaction of bromobenzene

 with phenylboronic acid using various NHC-Pd@MNPs nanomagnetic catalyst ratios

Entry	Base	Solvent	Tem- perature (°C)	Pd (mol%)	Yield (%) ^a
1	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	0.01	20
2	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	0.02	45
3	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	0.05	60
4	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	0.07	70
5	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	0.10	85
6	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	0.15	95
7	K_2CO_3	EtOH:H ₂ O (1:1)	70	0.20	95

Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), base (2.2 mmol) and solvent (5 mL) in air

^aIsolated yieldafter separation by column chromatography; average of two runs

3.3.2 Effect of Base on Suzuki–Miyaura cross-Coupling Reactions

The effect of bases on the efficiency of the NHC-Pd@ MNPs nanomagnetic catalyst in the Suzuki–Miyaura crosscoupling reaction of bromobenzene and phenylboronic acid was investigated by employing various bases (Table 3). Among the bases employed (K_2CO_3 , Na_2CO_3 , KF, NaOH, KOH, Na_3PO_4 and $CsCO_3$), K_2CO_3 , Na_2CO_3 , KF, Na_3PO_4 and $CsCO_3$ were found to be rather effective (Table 3, entries 1–3, 6 and 7). However, using bases like NaOH and KOH led to lower conversion (Table 3, entries 4 and 5).

3.3.3 Effect of Temperature on Suzuki– Miyaura cross-Coupling Reactions

It is also found that with the NHC-Pd@MNPs nanomagnetic catalyst, the reaction temperature has a great influence



Fig. 10 Plots depicting yields of Suzuki–Miyaura cross-coupling products against varying a temperatures, b time, and c catalyst ratio

Table 7	Suzuki-Miyaura	cross-coupling	reactions betw	veen aryl halio	les with phen	ylboronic acid	catalyzed by	NHC-Pd@MNPs	nanomagnetic
catalyst									

	\sim NHC-Pd@MNPs, K ₂ CO ₃							
	$R_1 = A + (HO)_2 B$	EtOH:H ₂ O (1:1)), 70 °C					
Entry	Aryl halide	Product	Time (h)	Yield (%) ^b				
1	H	н	1	95				
2	H	н	3	88				
3	H ₃ C Br	H ₃ C	1	72				
4	NC	NC	2	90				
5	H ₂ N Br	H ₂ N	4	85				
6	H J Br	н	4	82				
7	Br	н	18	45				
8	CI O H	H N N N N N N N N N N N N N N N N N N N	24	-				
9	O ₂ N Br	O ₂ N	1	91				
10	o Br	, C	1	90				

on the Suzuki–Miyaura cross-coupling reaction (Fig. 10a). As shown in Table 4, a high conversion was observed at temperature 70 and $80 \,^{\circ}$ C (Table 4, entries 5 and 6). At lower reaction temperatures (25, 40, 50 and $60 \,^{\circ}$ C)

(Table 4, entries 1–4), the yields were less, and at a high reaction temperature (100 °C) (Table 4, entry 8), the yield was decreased. Hence, all the reactions were carried out at 70 °C (Table 4, entry 5).

Table 7	(continued)
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Entry	Aryl halide	Product	Time (h)	Yield (%) ^b
11			0.17	98
12	HO	HO	1	80
13	HOCI	HO	16	40
14	O Br		0.5	94
15	CI		12	78
16	HO O	нобо	1	88
17	HOO	HOO	12	20
18	HO	но	5	85
19	F F	F	1	90

^aReaction conditions: Aryl halide (1.0 mmol), phenylboronic acid (1.1 mmol), NHC-Pd@MNPs (0.15 mol% Pd with respect to aryl halide), base (2.2 mmol) and solvent (5 mL) in air

^bIsolated yield after separation by column chromatography; average of two runs

3.3.4 Effect of Time on Suzuki–Miyaura cross-Coupling Reaction

To understand the rate of reaction with the prepared NHC-Pd@MNPs nanomagnetic catalyst, the model

Suzuki–Miyaura cross-coupling reaction of bromobenzene with phenylboronic acid was carried out at different time periods from 0.33 to 1.5 h (Fig. 10b). It is clear from the data obtained (Table 5) that with an increase in time, the conversion increased resulting in a higher yield; a



Fig. 11 The recycling efficiency of NHC-Pd@MNPs nanomagnetic catalyst in Suzuki–Miyaura cross-coupling reaction of bromobenzene and phenylboronic acid

 Table 8
 Recyclability of the NHC-Pd@MNPs nanomagnetic catalyst

 in Suzuki–Miyaura cross-coupling reactions of bromobenzene with

 phenylboronic acid

Entry	Base	Solvent	Tem- perature (°C)	Catalyst Run	% Yield ^a
1	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	Fresh	95
2	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	1st recycle	95
3	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	2nd recycle	95
4	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	3rd recycle	95
5	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	4th recycle	95
6	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	5th recycle	94
7	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	6th recycle	93
8	K ₂ CO ₃	EtOH:H ₂ O (1:1)	70	7th recycle	88
9	K_2CO_3	EtOH: $H_2O(1:1)$	70	8th recycle	81

Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), NHC-Pd@MNPs (0.15 mol% Pd with respect to aryl halide), base (2.2 mmol) and solvent (5 mL) in air

^aIsolated yield after separation by column chromatography; average of two runs

maximum yield was obtained in one hour (Table 5, entry 5). Also, a further increase in time beyond 1 h (1.5 h) does not improve the yield (Table 5, entry 6).

3.3.5 Effect of the Catalyst Ratioon Suzuki– Miyaura cross-Coupling Reactions

The quantity of catalyst plays an important role in Suzuki–Miyaura cross-coupling reactions. Therefore,

in order to find out the appropriate quantity of the NHC-Pd@MNPs nanomagnetic catalyst, we performed model Suzuki–Miyaura cross-coupling reactions of bromobenzene with phenylboronic acid with varying amounts of the NHC-Pd@MNPs nanomagnetic catalyst, starting from 0.01 mol% Pd to 0.20 mol% Pd (Fig. 10c). A higher conversion or maximum yield was obtained using 0.15 mol% Pd of the NHC-Pd@MNPs nanomagnetic catalyst, as shown in Table 6 (Table 6, entry 6). Furthermore, the use of higher quantities of the NHC-Pd@MNPs nanomagnetic catalyst (0.20 mol% Pd) does not increase the conversion (Table 6, entry 7).

Using the optimized reaction conditions, the NHC-Pd@ MNPs nanomagnetic catalyst was applied to a phenylboronic acid with a range of aryl bromides, aryl chlorides and aryl iodide. The results are tabulated in Table 7. All the bromides gave good to excellent yields except 2-bromobenzaldehyde (Table 7, entry 7). In detail, various electronwithdrawing and electron-donating groups such as -NH₂, -OH, -NO₂, -CH₃, -OCH₃, -CHO, -COCH₃ and -COOH on aryl bromide are well-tolerated affording the desired unsymmetric biaryls in good to excellent yields. Therefore, it can be concluded that the reaction yield was not influenced by the electronic properties of the substituent on the aryl bromides. However, aryl chlorides gave lesser yields compared with their bromide counter parts under the same reaction conditions (Table 7, entries 2, 8, 13, 15 and 17). On the other hand, iodoanisole gave 100% conversion in 10 min, as expected (Table 7, entry 11). These results confirmed the good performance of our NHC-Pd@MNPs nanomagnetic catalyst on Suzuki-Miyaura cross-coupling reactions. Furthermore, the selectivity of the prepared NHC-Pd@MNPs nanomagnetic catalyst was confirmed by conducting the Suzuki-Miyaura cross-coupling reaction using the optimized reaction conditions in the absence of aryl bromide. The homo-coupling biphenyl product was less than 2% even after maintaining the reaction for longer time. Thus, it is confirmed that the prepared NHC-Pd@ MNPs nanomagnetic catalyst is highly selective.

3.4 Catalyst Recyclability and Leaching Studies

Recyclability is an important factor to judge the sustainability of a catalyst. Therefore, the NHC-Pd@MNPs nanomagnetic catalyst was examined through the model Suzuki–Miyaura cross-coupling reaction between bromobenzene and phenylboronic acid. After completion of the reaction, the NHC-Pd@MNPs nanomagnetic catalyst can be conveniently and efficiently recovered from the reaction mixture using an external magnet, and can be used in the next run after washing with water followed by ethanol and drying. The results revealed that the NHC-Pd@ MNPs nanomagnetic catalyst can be reused without any

		Temp (C)	Time (h)	Y1eld (%)	Ref.
Iron oxide-Pd complex	DMF	50	12	77	[46]
MNPs-NHC-Pd(II)	EtOH: $H_2O(1:1)$	R.T	1	93	[57]
Fe ₃ O ₄ /SiO ₂ /HPG-OPPh ₂ -PNP	DMF:H ₂ O (1:1)	R.T	0.17	87	[58]
Catalyst-1	EtOH:H ₂ O (3:1)	70	12	87	[60]
Co/C-ROMP gel Pd	THF:H ₂ O (1:2)	65	12	92	[61]
Pd-Fe ₃ O ₄ NCS	Dimethoxyethane:H ₂ O (3:1)	Reflux	24	70	[62]
Pd-IL-NH ₂ /SiO ₂ /Fe ₃ O ₄	EtOH:H ₂ O (1:1)	80	5	87	[63]
Pd(II)NiFe ₂ O ₄	EtOH:H ₂ O (9:1)	80	6.5	93	[64]
G ₁ MNP	MeOH	60	5	89	[65]
MUA-Pd	DMF	90	12	92	[66]
Pd-MTAT	DMF:H ₂ O (1:5)	85	10	85	[67]
LDH-Pd(0)	1,4-Dioxane-H ₂ O (1:1)	80	10	94	[68]
Pd-MSN-IPr	Isopropyl alcohol	80	2	90	[69]
NHC-Pd@MNPs	EtOH: $H_2O(1:1)$	70	1	95	Present work
NHC-Pd@MNPs	EtOH:H ₂ O (1:1)	70	1	90	Present work
	Iron oxide-Pd complex MNPs-NHC-Pd(II) Fe ₃ O ₄ /SiO ₂ /HPG-OPPh ₂ -PNP Catalyst-1 Co/C-ROMP gel Pd Pd-Fe ₃ O ₄ NCS Pd-IL-NH ₂ /SiO ₂ /Fe ₃ O ₄ Pd(II)NiFe ₂ O ₄ G ₁ MNP MUA-Pd Pd-MTAT LDH-Pd(0) Pd-MSN-IPr NHC-Pd@MNPs NHC-Pd@MNPs	Iron oxide-Pd complex DMF MNPs-NHC-Pd(II) $EtOH:H_2O(1:1)$ $Fe_3O_4/SiO_2/HPG-OPPh_2$ -PNP DMF:H_2O(1:1) Catalyst-1 $EtOH:H_2O(3:1)$ Co/C-ROMP gel Pd THF:H_2O(1:2) Pd-Fe_3O_4 NCS Dimethoxyethane:H_2O(3:1) Pd-IL-NH_2/SiO_2/Fe_3O_4 $EtOH:H_2O(1:1)$ Pd(II)NiFe_2O_4 $EtOH:H_2O(9:1)$ G_1MNP MeOH MUA-Pd DMF:H_2O(1:5) LDH-Pd(0) 1,4-Dioxane-H_2O(1:1) Pd-MSN-IPr Isopropyl alcohol NHC-Pd@MNPs $EtOH:H_2O(1:1)$	Iron oxide-Pd complexDMF50MNPs-NHC-Pd(II)EtOH:H_2O (1:1)R.T $Fe_3O_4/SiO_2/HPG-OPPh_2$ -PNPDMF:H_2O (1:1)R.TCatalyst-1EtOH:H_2O (3:1)70Co/C-ROMP gel PdTHF:H_2O (1:2)65Pd-Fe_3O_4 NCSDimethoxyethane:H_2O (3:1)RefluxPd-IL-NH_2/SiO_2/Fe_3O_4EtOH:H_2O (1:1)80Pd(II)NiFe_2O_4EtOH:H_2O (9:1)80G_1MNPMeOH60MUA-PdDMF:H_2O (1:5)85LDH-Pd(0)1,4-Dioxane-H_2O (1:1)80Pd-MSN-IPrIsopropyl alcohol80NHC-Pd@MNPsEtOH:H_2O (1:1)70	Iron oxide-Pd complexDMF5012MNPs-NHC-Pd(II)EtOH:H_2O (1:1)R.T1 $Fe_3O_4/SiO_2/HPG-OPPh_2$ -PNPDMF:H_2O (1:1)R.T0.17Catalyst-1EtOH:H_2O (3:1)7012Co/C-ROMP gel PdTHF:H_2O (1:2)6512Pd-Fe_3O_4 NCSDimethoxyethane:H_2O (3:1)Reflux24Pd-IL-NH_2/SiO_2/Fe_3O_4EtOH:H_2O (1:1)805Pd(II)NiFe_2O_4EtOH:H_2O (9:1)806.5G_1MNPMeOH605MUA-PdDMF:H_2O (1:5)8510LDH-Pd(0)1,4-Dioxane-H_2O (1:1)802Pd-MSN-IPrIsopropyl alcohol802NHC-Pd@MNPsEtOH:H_2O (1:1)701	Iron oxide-Pd complexDMF501277MNPs-NHC-Pd(II)EtOH:H_2O (1:1)R.T193Fe_3O_4/SiO_2/HPG-OPPh_2-PNPDMF:H_2O (1:1)R.T0.1787Catalyst-1EtOH:H_2O (3:1)701287Co/C-ROMP gel PdTHF:H_2O (1:2)651292Pd-Fe_3O_4 NCSDimethoxyethane:H_2O (3:1)Reflux2470Pd-IL-NH_2/SiO_2/Fe_3O_4EtOH:H_2O (1:1)80587Pd(II)NiFe_O_4EtOH:H_2O (9:1)806.593G_1MNPMeOH60589MUA-PdDMF:H_2O (1:5)851085LDH-Pd(0)1,4-Dioxane-H_2O (1:1)801094Pd-MSN-IPrIsopropyl alcohol80290NHC-Pd@MNPsEtOH:H_2O (1:1)70195

 Table 9
 Comparison of results for the NHC-Pd@MNPs nanomagnetic catalyst with other catalysts for the Suzuki–Miyaura cross-coupling reaction between bromobenzene and phenylboronic acid

^aCoupling reaction between 4-bromoanisole and phenyl boronic acid

modification for up to five cycles, and no significant loss of activity was observed. In sixth recycle, NHC-Pd@MNPs nanomagnetic catalyst shown good activity but from seventh recycle onwards, a decrease in catalytic activity was observed (Fig. 11) (Table 8). The TEM, FESEM images and ATR-IR spectrum of five-times recycled NHC-Pd@ MNPs nanomagnetic catalyst was recorded. The TEM image (Fig. 5c) shows that there is no change in the morphology of the NHC-Pd@MNPs nanomagnetic catalyst after recycling up to five cycles which is further confirmed by the FESEM image (Fig. 6b). The ATR-IR spectrum (Fig. 2b) shows that the NHC-Pd@MNPs nanomagnetic catalyst is intact after recycling. Furthermore, the prepared NHC-Pd@MNPs nanomagnetic catalyst is stable at room temperature for more than 4 months. This was concluded by analyzing the performance of the NHC-Pd@ MNPs nanomagnetic catalyst after keeping it for more than 4 months at room temperature which showed no observable change in activity.

The leaching study of the NHC-Pd@MNPs nanomagnetic catalyst was also performed to understand the stability of the NHC-Pd@MNPs catalyst in the optimized reaction conditions. This study was done by magnetic separation of the NHC-Pd@MNPs catalyst after 10 min of reaction time, and the same reaction was further continued for more than 1 h and was monitored using TLC. Further conversion was not observed and the isolated yield was 60%. This proved that leaching of the NHC-Pd@MNPs nanomagnetic catalyst was not occurring and is stable in the chemical environment.

3.5 Comparison of Catalysts

Table 9 demonstrates a comparison of results for the NHC-Pd@MNPs nanomagnetic catalyst with other catalysts for the Suzuki–Miyaura cross-coupling reaction between bromobenzene and phenylboronic acid. Comparison of the results shows a better catalytic activity and shorter reaction time for the NHC-Pd@MNPs nanomagnetic catalyst in Suzuki–Miyaura cross-coupling reactions [60–69]. However, some of the major advantages of the NHC-Pd@ MNPs nanomagnetic catalyst are: (1) magnetically recoverable, (2) mild reaction conditions, (3) use of green solvents, (4) short reaction time, and (5) excellent selectivity. Also, the NHC-Pd@MNPs nanomagnetic catalyst can be synthesized by an incisive method using easily available chief chemicals under aerobic conditions, which do not require a sophisticated setup.

4 Conclusion

In summary, we have developed a new, practical, and economic NHC-Pd@MNPs nanomagnetic catalyst. The structure of the synthesized NHC-Pd@MNPs nanomagnetic catalyst was fully confirmed using AT-IR spectroscopy, UV–Visible spectrophotometry, ICP-AES, FESEM, EDS, TEM, XRD, TGA and BET analysis. The NHC-Pd@MNPs nanomagnetic catalyst showed extraordinary performance in Suzuki–Miyaura cross-coupling reactions. The NHC-Pd@MNPs nanomagnetic catalyst could be simply recovered from the reaction media using magnetic separation and could be reused at least five times without significant loss in activity. This approach could be used to prepare various new magneticnanoparticle supported N-heterocyclic carbene-palladium(II) nanomagnetic catalysts which could offer more opportunities for developing powerful and reusable catalysts for green organic synthesis.

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References

- 1. Zarnegar Z, Safari J (2014) New J Chem 38:4555
- 2. Corma A, Garcia H (2008) Top Catal 48:8
- Copèret C, Chabanas M, Arroman RPS, Basset JM (2003) Angew Chem Int Ed 42:156
- 4. Polshettiwar V, Varma RS (2010) Green Chem 12:743
- Shylesh S, SchünemannV, Thiel WR (2010) Angew Chem Int Ed 49:3428
- 6. Arduengo A, Harlow R, Kline M (1991) J Am Chem Soc 113:361
- 7. Herrmann WA, Elison M, Fischer J, Köcher C, Artus GRJ (1995) Angew Chem Int Ed 34:2371
- 8. Wang W, Wang F, Shi M (2010) Organometallics 29:928
- Alcarazo M, Stork T, Anoop A, Thiel W, Fürstner A (2010) Angew Chem Int Ed 49:2542
- Buscemi G, Basato M, Biffis A, Gennaro A, Isse AA, Natile MM, Tubaro C (2010) J Organometal Chem 695:2359
- 11. Frémont P, Marion N, Nolan SP (2009) Coord Chem Rev 253:862
- 12. Gonzalez SD, Marion N, Nolan SP (2009) Chem Rev 109:3612
- 13. Schuster O, Yang LR, Raubenheimer HG, Albrecht M (2009) Chem Rev 109:3445
- 14. Poyatos M, Mata JA, Peris E (2009) Chem Rev 109:3677
- 15. Enders D, Niemeier O, Henseler A (2007) Chem Rev 107:5606
- Hurst EC, Wilson K, Fairlamb IJS, Chechik V (2009) New J Chem 33:1837
- Lara P, Rivada-Wheelaghan O, Conejero S, Poteau R, Philippot K, Chaudret B (2011) Angew Chem Int Ed 50:12080
- 18. Vignolle J, Tilley TD (2009) Chem Commun 46:7230
- Hopkinson MN, Richter C, Schedler M, Glorius F (2014) Nature 510:485
- Jin Z, Guo SX, Qiu LL, Wu GP, Fang JX (2011) Appl Organomet Chem 25:502
- 21. Cekirdek S, Yaşar S, Özdemir I (2014) Appl Organomet Chem 28:423
- Karaca EÖ, Gürbüz N, Özdemir İ, Doucet H, Şahin O, Büyükgüngör O, Çetinkaya B (2015) Organometallics 34:2487
- Elazab H, Siamaki AR, Moussa S, Gupton BF, El-Shall MS (2015) Appl Catal A 491:58
- 24. Wilczewsk AZ, Misztalewsk I (2014) Organometallics 33:5203
- Ghotbinejad M, Khosropour AR, Mohammadpoor-Baltork I, Moghadam M, Tangestaninejad S, Mirkhani V 2014 J Mol Catal A 385:78
- Doğan Ö, Demir S, Özdemir İ, Çetinkaya B 2011 Appl Organomet Chem 25:163
- 27. Chen L, Xu Z, Dai H, Zhang S (2010) J Alloys Compd 497:221
- Jung JY, Kim JB, Taher A, Jin MJ (2009) Bull Korean Chem Soc 30:3082

- 29. Giudici RE, Hoveyda AH (2007) J Am Chem Soc 129:3824
- Kantchev EAB, Brien CJO, Organ MG (2007) Angew Chem Int Ed 46:2768
- 31. Polshettiwar V, Hesemann P, Moreau JJE (2007) Tetrahedron Lett 48:5363
- 32. Lebel H, Janes MK, Charette AB, Nolan SP (2004) J Am Chem Soc 126:5046
- Titcomb LR, Caddick S, Cloke FGN, Wilson DJ, McKerrecher D (2001) Chem Commun 15:1388
- Ranganath KVS, Kloesges J, Schäfer AH, Glorius F (2010) Angew Chem Int Ed 49:7786
- 35. Ranganath KVS, Schäfer AH, Glorius F (2011) Chem Cat Chem 3:1889
- Diederich F, Stang PJ (1998) Metal-catalyzed cross-coupling reactions. Wiley, Weinheim
- 37. Baur JA, Sinclair DA (2006) Nat Rev Drug Discov 5:493
- 38. Ke H, Chen X, Zou G (2014) Appl Organometal Chem 28:54
- Firouzabadi H, Iranpoor N, Gholinejad M, Akbari S, Jeddi N (2014) RSC Adv 4: 17060
- 40. Rostamnia S, Hossieni HG, Doustkhah E (2015) J Organometal Chem 791:18
- Chapman MR, Lake BRM, Pask CM, Nguyen BN, Willans CE (2015) Dalton Trans 44:15938
- 42. Serrano JL, Pérez J, García L, Sánchez G, García J, Lozano P, Zende V, Kapdi A (2015) Organometallics 34:522
- 43. Ranganath KVS, Glorius F (2011) Catal Sci Technol 1:13.
- Rahimi R, Maleki A, Maleki S, Morsali A, Rahimi MJ (2014) Solid State Sci 28:9
- 45. Stevens PD, Li G, Fan J, Yen M, Gao Y (2005) Chem Commun 35:4435
- Stevens PD, Fan J, Gardimalla HMR, Yen M, Gao Y (2005) Org Lett 72085
- 47. Zheng Y, Stevens PD, Gao Y (2006) J Org Chem 71:537
- Bordoloi A, Sahoo S, Lefebvre F, Halligudi SB (2008) J Catal 259:232
- Dadhania HN, Raval DK, Dadhania AN (2015) Catal Sci Technol 5:4806
- 50. Ghorbani-Choghamarani A, Azadi G (2016) Appl Organomet Chem 30:247
- 51. Behera SS, Patra JK, Pramanik K, Panda N, Thatoi H (2012) World J Nano Sci Eng 2:196
- 52. Wang X, Neissner R, Knopp D (2014) Sensors 14:21535
- Zhang J, Gan N, Chen S, PanM, Wu D, Cao Y (2015) J Chromatogr A 1401:24
- 54. Zhang Q, Su H, Luo J, Wei Y (2013) Catal Sci Technol 3:235
- Nehlig E, Waggeh B, MillotN, Lalatonne Y, Motte L, Guénin E (2015) Dalton Trans 44:501
- 56. Polshettiwar V, Varma RS (2009) Org Biomol Chem 7:37
- 57. Hajipour AR, Tadayoni NS, Khorsandi Z (2016) Appl Organomet Chem 30:590
- Du Q, Zhang W, Ma H, Zhang J, Zhou B, Li Y (2012) Tetrahedron 68:3577
- 59. Yang H, Wang Y, Qin Y, Chong Y, Yang Q, Li G, Zhang L, Li W 2011 Green Chem 13:1352
- 60. Wang Z, YuY, Zhang YX, Li SZ, Qian H, Lin ZY (2015) Green Chem 17:413
- Schätz A, Long TR, Grass RN, Stark WJ, Hanson PR, Reiser O (2010) Adv Funct Mater 20:4323
- Jang Y, Chung J, Kim S, Jun SW, Kim BH, Lee DW, Kim BM, Hyeon T (2011) Phys Chem Chem Phys 13:2512
- 63. Wang J, Xu B, Sun H, Song G (2013) Tetrahedron lett 54:238
- 64. Singh AS, Shelkar RS, Nagarkar JM (2015) Catal lett 145:723
- Liao Y, He L, Huang J, Zhang J, Zhuang L, Shen H, Su CY (2010) ACS Appl Mater Interfaces 2:2333

- Cargnello M, Weider NL, Canton P, Montini T, Giambastiani G, Benedetti A, Gorte RJ, Fornasiero P (2011) Chem Mater 23:3961
- 67. Modak A, Mondal J, Sasidharan M, Bhaumik A (2011) Green Chem 13:1317
- 68. Singha S, Sahoo M, Parida KM (2011) Dalton Trans 40:7130
- 69. YangH, Wang Y, Qin Y, Chong Y, Yang Q, Li G, Zhang L, Li W (2011) Green Chem 13:1352.