

N-heterocyclic carbene-palladium(II) complex supported on magnetic mesoporous silica for Heck cross-coupling reaction

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Yagoub Mansoori, Department of Applied Chemistry, Faculty of Science, University of Mohaghegh Ardabili, Ardabil, 56199-11367, Iran. Email: ya_mansoori@yahoo.com; ya_mansoori@uma.ac.ir Magnetic mesoporous silica was prepared via embedding magnetite nanoparticles between channels of mesoporous silica (SBA-15). The prepared composite (Fe₃O₄@SiO₂-SBA) was then reacted with 3-chloropropyltriethoxysilane, sodium imidazolide and 2-bromopyridine to give 3-(pyridin-2-yl)-1Himidazol-3-iumpropyl-functionalized Fe₃O₄@SiO₂-SBA as a supported pincer ligand for Pd(II). The functionalized magnetic mesoporous silica was further reacted with [PdCl₂(SMe₂)₂] to produce a supported N-heterocyclic carbene-Pd(II) complex. The obtained catalyst was characterized using Fourier transform infrared spectroscopy, scanning electron microscopy, energy-dispersive X-ray analysis, vibrating sample magnetometry, Brunauer–Emmett–Teller surface area measurement and X-ray diffraction. The amount of the loaded complex was 80.3 mg g^{-1} , as calculated through thermogravimetric analysis. The formation of the ordered mesoporous structure of SBA-15 was confirmed using low-angle X-ray diffraction and transmission electron microscopy. Also, X-ray photoelectron spectroscopy confirmed the presence of the Pd(II) complex on the magnetic support. The prepared magnetic catalyst was then effectively used in the coupling reaction of olefins with aryl halides, i.e. the Heck reaction, in the presence of a base. The reaction parameters, such as solvent, base, temperature, amount of catalyst and reactant ratio, were optimized by choosing the coupling reaction of 1-bromonaphthalene and styrene as a model Heck reaction. N-Methylpyrrolidone as solvent, 0.25 mol% catalyst, K₂CO₃ as base, reaction temperature of 120°C and ultrasonication of the catalyst for 10 min before use provided the best conditions for the Heck cross-coupling reaction. The best results were observed for aryl bromides and iodides while aryl chlorides were found to be less reactive. The catalyst exhibited noticeable stability and reusability.

KEYWORDS

Heck reaction, heterogeneous catalyst, magnetic mesoporous silica, NHC-Pd(II) complex

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1 | INTRODUCTION

In 2010, the Nobel Prize for Chemistry was awarded to Heck, Negishi and Suzuki for their research on palladium-catalysed cross-coupling reactions in organic synthesis since these reactions are strategically very important and powerful for the formation of C—C bonds.^[1] In recent years, intensive studies have focused on the preparation and supporting of palladium complexes with various types of ligands as effective catalysts for coupling reactions. Such efforts have resulted in improvements in the efficiency of organic syntheses and a reduction in process time, reaction costs and generation of byproducts.^[2] These reactions have a great potential for industrial applications; however, due to the properties and activities of the existing catalysts, limited industrial applications have been observed for the Heck reaction.^[3] On the other hand, many researchers have noted that the Heck coupling reaction is regioselective. For example, Hallberg et al. showed that the regiochemistry of enol ether arylation can be controlled by various parameters, such as the electronic nature and halogen type of its aromatic ring.^[4] In addition to regioselectivity and industrial applicability, the high atomic economy and low-cost reagents of palladium-catalysed C-H functionalization in C-C coupling reactions have led to the exploration of many to Pd complexes in modern organic chemistry. Developing highly regioselective reactions and enhancing the catalytic activity by using particular ligands are the focal points of most recent studies in this field.^[5]

Highly ordered mesoporous silica materials have attracted a considerable deal of attention in the various applications, such as diagnosis, drug delivery, extraction and hyperthermia. Their non-toxic nature, high surface area (700 to 1200 m² g⁻¹), abundant Si-OH bonds, tunable volume and pore diameter (2 to 50 nm) and potency of surface modification mean that they are attractive candidates for coating and catalyst support purposes. An example of such materials is SBA-15, which can present high hydrothermal stability, large pore size (4.6 to 10.0 nm), two-dimensional hexagonal (p6mm) mesostructure and thick uniform silica walls (31 to 64 Å). For these reasons, SBA-15 has been considered for simple internal surface functionalization and release of large molecules.^[6–9] For example, Lazar et al. designed a highly efficient reusable heterogeneous catalyst using SBA-15, i.e. Pd(II)-DHBP@SBA-15, for arylation through the Heck reaction and hydrogenation of alkenes. Their supported catalyst obtained via anchoring a 2,2-dihydroxybenwas zopheneone ligand onto amino-functionalized SBA-15 and subsequent metalation by Pd(II). Their obtained solid catalyst was recycled effectively and reused several times without any significant loss of activity.^[10]

Anchoring of catalysts on magnetic nanoparticles (MNPs) has been the focus of many research activities in recent years.^[11-14] MNPs have advantages of non-toxicity, high dispersibility, biocompatibility, a noticeably high surface-to-volume ratio, high coercivity, superparamagnetic properties, great extraction efficiency and convenient separation.^[15,16] In addition, MNP-supported catalysts can be easily and rapidly collected from various reaction mixtures by means of an external magnet.

Although bare MNPs have been reported as catalyst supports,^[17,18] they have an intrinsic tendency towards agglomeration. In order to overcome this limitation, it is recommended to use MNPs in the form of composites. Various materials, such as silica, oleic acid and polystyrene, have been used for this purpose. Among all reported matrices, mesoporous silica has been more emphasized due to its biocompatibility,^[19] high surface area, large pore size and the other aforementioned advantages.

Combination of MNPs and mesoporous silica provides the advantages of both high surface area and magnetic properties. That is why many researchers have investigated the modification of MNPs by mesoporous silica materials, e.g. SBA-15 and various kinds of MCMs, in recent years.^[18,20,21] Incorporation of MNPs within the channels of SBA-15 leads to the formation of Fe_xO_y $\otimes SBA-15$ particles that can be employed as magnetically retrievable catalyst supports.^[22,23] Application of such support material was reported by Tai et al., who studied the synthesis of magnetic core-shell structures of mesoporous silica functionalized with sulfonic acid and used the obtained nanoparticles for catalysis of esterification. Their porous magnetic nanocomposites showed high activity towards esterification of propionic acid, in addition to facile recovery and re-use.^[24] Also, Snoussi et al. synthesized a core-double shell nanocomposite, i.e. Fe₃O₄@NH₂-mesoporous silica@polypyrrole/ Pd, via a sonochemical procedure. The catalytic activity of their obtained magnetic material was assessed in the reduction of 4-nitrophenol to 4-aminophenol, which gave a yield of above 94%, and in the degradation of methyl orange in aqueous media (with 99% yield).^[25] In a recent study, Keypour et al. synthesized a Pd(II)-Schiff base complex supported on MNPs as a retrievable heterogeneous catalyst. Their supported catalyst was used in the Suzuki cross-coupling reaction of various aryl halides (I, Br, and Cl) with phenylboronic acid and in the Heck coupling reaction of aryl halides (I and Br) with styrene.^[26]

Though mesoporous silica composites have been widely applied to coupling reactions, limited studies have been reported about anchoring homogeneous catalysts on mesoporous magnetic silica for C—C coupling reactions.

One of the rare examples of such research is the study of Nikoorazam *et al.*, who synthesized and characterized a Pd(0)–Schiff base complex supported on magnetic nanoporous MCM-41 as a catalyst for the Suzuki and Heck reactions. Their catalyst could be easily recovered from the reaction mixture using an external magnet and reused several times.^[27]

With respect to the advantages and drawbacks of the mentioned materials, herein, we report the synthesis and characterization of a novel N-heterocyclic carbene (NHC)–Pd(II) complex anchored on Fe₃O₄@SiO₂-SBA. The obtained retrievable magnetic catalyst showed excellent efficiency in the Heck reaction. To the best of our knowledge, the present study is the first report of the use of Fe₃O₄@SiO₂-SBA as a magnetic support for the Heck reaction.

2 | EXPERIMENTAL

2.1 | Instrumentation

NMR spectra were obtained with a Bruker Avance 250 MHz spectrometer using tetramethylsilane. Fourier transform infrared (FT-IR) spectra were recorded with a PerkinElmer RXI spectrophotometer using KBr. Thermogravimetric analysis (TGA) was conducted with a Linseis STA PT 1000 instrument using a scanning rate of 10°C min⁻¹. The inductively coupled plasma optical emission spectrometry (ICP-OES) technique (Perkin-Elmer, Optima 5300 DV) was employed for the determination of the amount of palladium on the supported NHC-Pd(II) complex. Wide angle X-ray diffraction (XRD) and low-angle XRD in the 2θ ranges $10-80^{\circ}$ and 0.7-10° were conducted with Philips PW1730 (scanning rate of 0.01° min⁻¹) and Philips X-Pro (scanning rate of 1° min⁻¹) instruments at room temperature, respectively. Both instruments were equipped with an X-ray radiation source using Cu K_{α} ($\lambda = 0.15406$ nm). Scanning electron microscopy (SEM) images were obtained with a LEO 1430VP instrument. A vibrating sample magnetometry (VSM) instrument (Maghnatis Danesh-pajooh Kashan Co. Iran) with a maximum magnetic field of 10 kOe was used for magnetization measurements at room temperature. Transmission electron microscopy (TEM) images of the supported NHC-Pd(II) complex were obtained with a LEO 912 AB microscope with an acceleration voltage of 120 kV. Multipoint nitrogen adsorption-desorption analysis according to the Brunauer-Emmett-Teller (BET) method was performed at -197.018°C using a TriStar II plus Micromeritics automated gas adsorption analyser. Energy-dispersive X-ray (EDX) microanalysis was performed with a QUANTAX QX2 (RONTEC, Germany). X-ray photoelectron spectroscopy (XPS) was carried out with a Kratos Axis Ultra DLD electron spectrometer using a monochromated Al K_{α} source operated at 150 W. Analyser pass energies of 160 and 20 eV were applied for acquiring wide spectra and individual photoelectron lines, respectively. The spectrometer charge neutralization system was used for stabilization of surface potential. The Si 2p line of silica, set at 103.3 eV, was used as reference of the binding energy scale. Kratos software was used to process the spectra. Powder samples were hand-pressed into pellets directly on a sample holder using a clean Ni spatula. Quantitative GC analyses were performed with an Agilent 7890 instrument using a capillary column in conjunction with a flame ionization detector. Column temperature was programmed between 180 and 200°C (2°C min⁻¹). Nitrogen was used as a carrier gas at a flow rate of 20 ml min⁻¹.

2.2 | Materials

MNPs,^[28] Fe_3O_4 @SiO₂-SBA^[29] and *trans*-[Pd(Cl)₂ (SMe₂)₂] complex^[30] were prepared according to the literature. 3-Chloropropyltrimethoxysilane (CPTS) and pluronic P-123 were obtained from Exir (Austria) and used as received. All solvents were of laboratory grade and dried according to procedures described in the literature.^[31] The other laboratory-grade chemicals were obtained from Merck and used without further purification.

2.3 | Functionalization of Fe₃O₄@SiO₂-SBA with CPTS

The MNPs of Fe_3O_4 @SiO₂-SBA (1.000 g) were dispersed in 40 ml toluene. Then, CPTS (4.1 ml, 17.1 mmol) was added to the suspension dropwise and the reaction mixture was refluxed for 24 h. The functionalized magnetic mesoporous silica was decanted magnetically, washed with methanol and acetone several times and then dried in a vacuum oven at 45°C.

2.4 | Synthesis of Fe₃O₄@SiO₂-SBA-(CH₂)₃imidazole

Sodium hydride (0.410 g, 17.1 mmol) was added to a magnetically stirred solution of imidazole (1.160 g, 17.1 mmol in 25 ml of sodium-dried toluene), and stirred for 30 min under an argon atmosphere at room temperature to give sodium imidazolide. Then, $Fe_3O_4@SiO_2-SBA-(CH_2)_3-Cl$ (1.000 g) was added and the mixture was refluxed under an argon atmosphere for 24 h. The imidazole-functionalized

magnetic mesoporous silica was decanted magnetically, washed with ethanol several times and then dried in a vacuum oven at 45°C.

2.5 | Synthesis of 3-(pyridin-2-yl)-1*H*imidazol-3-iumpropyl (PIP)-functionalized Fe₃O₄@SiO₂-SBA

The synthesized Fe₃O₄@SiO₂-SBA-(CH₂)₃-imidazole and 2-bromopyridine (0.770 ml, 8.07 mmol) were stirred for 20 h at 160°C. The mixture was then cooled to room temperature and the resultant functionalized magnetic mesoporous silica was washed several times with the Et₂O-CH₂Cl₂ mixture (80/20, 20 ml) and decanted magnetically. The obtained MNPs were then dried in a vacuum oven at 45°C.

2.6 | Synthesis of supported NHC-Pd(II) complex

PIP-functionalized Fe₃O₄@SiO₂-SBA and *trans*-[Pd(Cl)₂ (SMe₂)₂] were dispersed in 20 ml of dry tetrahydrofuran (THF). Then, a THF solution of potassium *t*-butoxide (0.030 g, 0.27 mmol) was added to the mixture at -80° C under continuous stirring. The reaction mixture was warmed to room temperature over 1.5 h and stirred for another 12 h. The supported NHC–Pd(II) complex was decanted magnetically and washed with Et₂O–CH₂Cl₂ mixture (80/20) several times. In order to replace the chloride ion of the supported complex with bromide ion, the obtained MNPs were stirred for 4 h in 20 ml of a dry acetone solution containing NaBr (0.125 g, 1.22 mmol). The final product was separated using an external magnet, washed with acetone and dried in a vacuum oven at 45°C.^[32]

2.7 | Heck coupling reaction

In a 25 ml round-bottom flask, the supported NHC–Pd(II) complex was dispersed in 1 ml of dry *N*-methylpyrrolidone (NMP) with 8 min of ultrasonication. Aryl halide (1.0 mmol), olefin (1.2 mmol) and K_2CO_3 (1.2 mmol) were then added to the catalyst suspension and the reaction mixture was stirred at 120°C. The optimal amount of Pd(II) was 0.25 mol% of aryl halide. The progress of the reaction was monitored by TLC. After completion of the residue was analysed using GC in order to determine its final composition. Further purification for NMR analysis was achieved by conducting chromatography on glass plates using silica gel as the stationary phase.

3 | RESULTS AND DISCUSSION

3.1 | Catalyst synthesis and characterization

The MNPs were prepared by a co-precipitation method and then incorporated between the channels of SBA-15. The as-prepared magnetic mesoporous particles were then functionalized with PIP–Pd(II) complex^[32] to afford the supported NHC–Pd(II) complex (Scheme 1).

The FT-IR spectra of MNPs, MNP@SiO₂-SBA and supported NHC-Pd(II) complex are shown in Figure 1. In all spectra, the presence of ν_{as} (Si—O—Si) band at 1110 cm⁻¹ and the characteristic strong peak of magnetite at 589 cm⁻¹ reveal the embedding of MNPs between SBA-15 channels.^[33] In the spectrum of the NHC-Pd(II) complex (Figure 1c), the bands related to imidazole ring appear at 1854 and 1448 cm⁻¹. Also, the C&dbond;N stretching frequency, probably somewhat coupled with the pyridine ring vibration, is observed at 1624 cm⁻¹.^[34]

The assigned ¹³C CP-MAS NMR spectrum of the supported catalyst is shown in Figure 2. The C-2 and C-6 carbons of pyridine ring (C_a and C_b) appear at 146.2 and 148.1 ppm, respectively. The C-2 atom of five-membered ring (C_c) and C-4 atom of pyridine ring (C_d) are seen at 137.5 and 139.2 ppm, respectively. The remaining aromatic carbon atoms, C-4 and C-5 carbons of five-membered ring (C_h and C_g), are observed at 111.7–130.0 ppm. In the aliphatic region, the propyl carbons appear at 50.3 ppm (C_i), 23.2 ppm (C_j) and 7.5 ppm (C_k).^[35,36]

The amount of loaded Pd(II) (0.25 mmol g⁻¹; 2.64 wt%) was measured by ICP-OES. TGA was used to estimate the quantity of the loaded Pd(II) complex. Removal of physically and chemically adsorbed H₂O molecules is shown by a mass loss of about 3.17% for MNP@SiO₂-SBA from ambient temperature to 690°C (Figure 3a). Under the same conditions, a very distinct mass loss of about 11.2% is observed for the supported NHC-Pd(II) complex due to the thermal breakdown of the complex (Figure 3b). The difference between these two values ($\Delta m = 8.03\%$) can be attributed to the amount of complex loaded onto MNP@SiO₂-SBA (8.03% or 80.3 mg g⁻¹ of magnetic mesoporous silica).

The SEM images of the MNPs and supported catalyst are shown in Figure 4. The MNPs have a uniform spherical morphology with diameters below 50 nm (Figure 4a). Also, the particles of the supported catalyst have a uniform size distribution and possess diameters greater than 100 nm (Figure 4b). These particles seem to be aggregated possibly due to the very high hydrophilicity of the mesoporous silica and moisture adsorption.^[37]



SCHEME 1 Synthesis of the supported NHC-Pd(II) complex



FIGURE 1 FT-IR spectra (KBr): (a) MNPs; (b) MNP@SiO₂-SBA; (c) supported NHC-Pd(II) complex



FIGURE 2 Solid-state ¹³C NMR spectrum of supported NHC-Pd(II) complex

The XRD patterns of the bare MNPs and supported NHC–Pd(II) complex are presented in Figure 5 and outline the characteristic peaks of magnetite. Therefore, Figure 5a confirms the formation of cubic magnetite nanoparticles (JCPDS file no. 01-1111) with the Fd-3m space group.^[38] Furthermore, the crystal structure of magnetite remains unchanged in the final product. The attenuation of the diffraction peaks can be attributed to the embedding of MNPs between mesoporous silica channels (Figure 5b). The observed peaks at $2\theta = 39^{\circ}$ and 47° may be related to the formation of palladium nanoparticles (111 and 200 hkl, respectively), which has been reported for the unsupported catalyst.^[32]

The low-angle XRD pattern of MNP@SiO2@SBA is depicted in Figure 6a. This pattern displays a wellrecognized diffraction peak at $2\theta = 1.06^{\circ}$ corresponding to the (100) diffraction, characteristic of a well-ordered two-dimensional hexagonal (p6mm) mesoporous structure.^[39] Pure SBA-15 sample exhibits two other peaks corresponding to (110) and (200) diffractions at $2\theta = 1.58^{\circ}$ and 1.82° .^[40] Since the introduction of magnetite between the channels of mesoporous silica decreases the ordering of SBA-15, the peaks corresponding these diffractions are absent in the pattern of MNP@SiO₂-SBA, as can be seen in the literature.^[41,42] The retention of the peak corresponding to the (100) diffraction in the low-angle XRD pattern of the supported NHC-Pd(II) complex (Figure 6b) indicates that the ordered mesoporous structure was maintained in the magnetic solid catalyst. Attenuation of the peaks is probably due to the difference in the scattering contrasts of the pores and walls and formation of the Pd(II) complex inside the channels of MNP@SiO2@SBA. The shift of the diffraction peak can be attributed to the functionalization of the interior walls of the pores by the complex.^[43]

The ordered mesoporous structure of SBA-15 that is observed using low-angle XRD was further confirmed by TEM (Figure 7). The TEM images of MNP@SiO₂@SBA show highly ordered arrays of one-



FIGURE 3 TGA thermograms (nitrogen atmosphere, scan rate of 10°C min⁻¹): (a) MNP@SiO₂-SBA; (b) supported NHC-Pd(II) complex





FIGURE 6 Low-angle powder XRD patterns: (a) MNP@SiO₂-SBA; (b) supported NHC-Pd(II) complex



(b)

FIGURE 4 SEM images: (a) MNPs; (b) supported NHC-Pd(II) complex



FIGURE 5 Wide-angle powder XRD patterns: (a) MNPs; (b) supported NHC-Pd(II) complex

dimensional mesoporous channels. As illustrated in Figure 7, the Fe_3O_4 nanoparticles of 20 to 50 nm in diameter are dispersed between the channels.

The qualitative elemental composition of the supported NHC-Pd(II) complex was determined using EDX analysis at random points on the surface. The weight and atomic percentages of the elements present in the samples are listed in Table 1. This measurement confirmed the presence of palladium atoms together with iron, carbon, nitrogen, oxygen, bromine and silicon atoms.

The magnetization curves of MNPs, MNP@SiO₂ and the supported NHC-Pd(II) complex are shown in Figure 8 and Table 2 summarizes the results. As can be seen, the saturation magnetization values (M_s) of the prepared materials are in the range 6.83 to 78.14 emu g⁻¹. These values are less than those reported for bulk magnetite particles (92 to 100 emu g⁻¹) due to the superparamagnetic behaviour that can be observed for singledomain MNPs below a critical size.^[44] Embedding of the MNPs between the non-magnetic mesoporous silica channels of SBA is responsible for decreasing the M_s values. Moreover, small-field coercivity of the supported NHC– Pd(II) complex ($H_c = 36.81$ Oe, $M_r = 0.44$ emu g⁻¹ and $M_r/M_s = 0.06$) shows that the supported catalyst particles are superparamagnetic.^[45]

The BET surface areas, pore volumes and average pore sizes of the magnetic mesoporous silica and the supported catalyst are summarized in Table 3. The nitrogen adsorption–desorption isotherms of MNP@SiO₂-SBA and the supported NHC–Pd(II) complex are shown in Figure 9. As can be seen, MNP@SiO₂-SBA exhibits a typical type-IV curve with an H2 hysteresis loop.^[46] The average pore diameter of MNP@SiO₂-SBA is 7.63 nm, the average pore volume is 0.77 cm³ g⁻¹ and the BET surface

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FIGURE 7 TEM images of MNP@SiO2-SBA

TABLE 1 Amounts of various elements present in supported

 NHC-Pd(II) complex

Element	Amount (wt%)	Amount (at%)
Carbon	0.75	1.35
Nitrogen	4.31	6.67
Oxygen	43.81	59.40
Sodium	6.50	6.14
Silicon	23.02	17.78
Iron	13.16	5.11
Bromine	1.30	0.35
Palladium	2.58	0.53

area is 483 m² g⁻¹. The corresponding values for the supported catalyst are 6.56 nm, 0.20 cm³ g⁻¹ and 105 m² g⁻¹. This can be an indication that the PIP–Pd(II) complex has been successfully supported into the pores. The obtained results indicate that MNPs do not block the intrachannel space, allowing molecules to enter the channels for subsequent modifications. Moreover, the value found for the pore diameter of the final catalyst is in the range of accepted values for mesoporous materials (2–50 nm).^[46] The sharp increase of *P*/*P*⁰ from 0.5 to 1.0 and the narrow size distribution (7.63 nm) highlight the formation of a highly ordered mesoporous material with hexagonal cylindrical channels.^[22]



FIGURE 8 Magnetization curves for MNPs, MNP@SiO2 and supported NHC-Pd(II) complex

TABLE 2 Magnetic properties of prepared materials

Sample	$M_{\rm s}$ (emu g ⁻¹) ^a	<i>M</i> _r (emu g ⁻¹) ^b	H _c (Oe) ^c	${M_{ m r}}/{{M_{ m s}}^{ m d}}$
MNPs	78.14	4.03	18.62	0.05
MNP@SiO ₂	34.52	1.91	22.24	0.06
Supported NHC complex	6.83	0.44	36.81	0.06

^aSaturation magnetization.

^bRemanent magnetization.

^cCoercive force.

^dRemanence ratio.

TABLE 3 Physical properties of prepared materials

Sample	D _{pore} (nm)	Pore volume (cm ³ g ⁻¹)	$S_{\rm BET}$ (m ² g ⁻¹)
MNP@SiO ₂ -SBA	7.63	0.77	483
Supported NHC-Pd(II) complex	6.56	0.20	105



FIGURE 9 Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) of MNP@SiO₂-SBA and supported NHC-Pd(II) complex



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FIGURE 10 High-resolution XPS spectra of supported NHC-Pd(II) complex: (a) C 1s region; (b) Pd $3d_{5/2}$ and Pd $3d_{3/2}$ core levels; (c) N 1s region

In the C 1s XPS spectrum of the supported NHC-Pd(II) complex (Figure 10a), five main components are observed. These components have binding energies at 284.8, 285.8, 286.8, 288.3 and 289.6 eV and can be assigned to carbon in C—C/C—H, C—N(C=N), C—O, O—C=O and carbonate bonds, respectively. The incomplete chemical calcination of pluronic P-123 might be responsible for the

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appearance of the C—O bonds.^[25] Figure 10b shows the XPS spectrum of the Pd 3d core level of the supported catalyst. Two Pd 3d doublets located at 343.2 and 338.0 eV (Pd 3d_{5/2}), and 341.0 and 335.8 eV (Pd 3d_{3/2}) confirm that both Pd(II) and Pd(0) species are present in the sample.^[47,48] Appearance and increase in intensity of Pd 3d doublet corresponding to Pd(0) were observed from XPS measurements followed by a decrease in Pd(II) doublet intensity. This effect seems to be induced by X-ray photon bombardment together with low-energy electrons used for the surface charge compensation.^[49] Lastly, the N 1s region, Figure 10c, contains two components at binding energies of 399.4 and 400.9 eV, which may be assigned to the nitrogen atom in the pyridine ring and to the partially positively charged nitrogen atoms in five-membered ring, respectively.

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3.2 | Heck coupling reaction

3.2.1 | Optimization of reaction conditions

The reaction conditions were optimized by focusing on the coupling reaction of 1-bromonaphthalene and styrene, as model substrates for the Heck reaction, and varying the reaction parameters including solvent, catalyst dosage, base, reactant molar ratio, reaction temperature and sonication of the magnetic catalyst prior to use. The results are presented in Table 4. After a careful screening of various solvents (entries 1–7), NMP turned out to be the best by giving the highest yield of the coupling product (entry 7, 54% yield). Then, the effect of catalyst loading was optimized. The best conversion was observed using 0.25 mol% catalyst (entry 11, 90% yield). Evaluation

TABLE 4 Optimization of conditions for Heck reaction^a

Br + Cat. Base Solvent. Δ								
Entry	Solvent	Pd (mol%)	Base	ArX:styrene	Temperature (°C)	Conversion (%) ^b	TON ^c /TOF (h ⁻¹) ^d	
1	Ethyl acetate	0.13	K ₂ CO ₃	1:1	e	Trace	—	
2	Acetone	0.13	K ₂ CO ₃	1:1	e	43	331/110	
3	CHCl ₃	0.13	K ₂ CO ₃	1:1	e	Trace	_	
4	CH ₃ CN	0.13	K ₂ CO ₃	1:1	e	Trace	—	
5	DMF	0.13	K ₂ CO ₃	1:1	120	Trace	—	
6	DMAc	0.13	K ₂ CO ₃	1:1	120	15	116/39	
7	NMP	0.13	K ₂ CO ₃	1:1	120	54	416/139	
8	NMP	0.22	K ₂ CO ₃	1:1	120	85	386/129	
9	NMP	0.25	K ₂ CO ₃	1:1	80	82	328/109	
10	NMP	0.25	K ₂ CO ₃	1:1	100	88	352/117	
11	NMP	0.25	K ₂ CO ₃	1:1	120	90	360/120	
12	NMP	0.25	K ₂ CO ₃	1:1	150	90	360/120	
13	NMP	0.25	Free	1:1	120	70	278/93	
14	NMP	0.25	Et ₃ N	1:1	120	46	184/61	
15	NMP	0.25	CsF	1:1	120	86	343/115	
16	NMP	0.25	Pyridine	1:1	120	71	284/95	
17	NMP	0.25	NaOAc	1:1	120	63	252/84	
18	NMP	0.25	K ₂ CO ₃	1:1.2	120	92	368/123	
19^{f}	NMP	0.25	K ₂ CO ₃	1:1.2	120	96	384/128	

^aReaction conditions: 1-bromonaphthalene (1.0 mmol), styrene (1.0 mmol), solvent (1 ml), base (1.2 mmol) and reaction time 3 h.

^bDetermined by GC analysis.

^cTON = number of moles of desired product/number of moles of metal active sites.

 d TOF = number of moles of reactant converted/(number of moles of metal active sites × time in hours).

^eReflux temperature.

^fSupported NHC-Pd(II) complex was sonicated in an ultrasonic bath for 10 min before reaction.

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TABLE 5 Heck reaction of aryl halide swith olefins catalysed by supported NHC-Pd(II) complex^a

$R' + R' \frac{\text{Cat., } K_2\text{CO}_3}{\text{NMP, } 120^{\circ}\text{C}} R'$								
				M.p. (°C	:)			
Entry	Aryl halide	Olefin	Product	Found	Reported	Time (h)	TON/TOF (h ⁻¹)	Conversion (%)
1	Br			74–76	76–78 ^[50]	2.5	360/144	90
2	Br	o o	J. J	Oil	Oil ^[51]	2.0	384/192	96
3		o o		Oil	Oil ^[52]	1.5	396/264	99
4	Br	o o	y y y y y y y y y y y y y y y y y y y	108–110	105–108 ^[53]	3.0	393/131	98
5		0 0		89–91	88–89 ^[52]	1.5	401/267	100
6			C C C C C C C C C C C C C C C C C C C	37–39	36-38 ^[52]	2.0	396/198	99
7	O Br			145–147	148–150 ^[47]	2.5	395/158	99
8				135–137	135–137 ^[47]	2.0	396/198	99
9				118-120	118.5–121.5 ^[54]	2.0	384/192	96
10	Br	o o	° °	Oil	Oil ^[52]	2.0	396/198	99
11	Br			71–73	70-71 ^[47]	3.0	384/128	96
12	Br	0		37–39	36-38 ^[52]	2.5	395/158	99
13	Br			118-120	118.5–121.5 ^[54]	2.5	385/154	96



^aReaction conditions: aryl halide (1.0 mmol), olefin (1.2 mmol), solvent (1 ml) and base (1.2 mmol).

of the effect of various reaction temperatures and bases (entries 9–17) showed that the highest advancement of the coupling reaction was for 120°C and K_2CO_3 as base (entry 11). It should be added that the product yield was not satisfactory in the absence of any base (entry 13, 70% yield). Also, the molar ratio of ArX/olefin was optimized and the best result was observed using a 1:1.2 molar ratio (entry 18, 92% yield). Finally, it was observed that sonicating the magnetic supported catalyst for 10 min improves the progress of the reaction (entry 19, 96% yield).

After optimizing the reaction conditions, the scope of the reaction was investigated by applying the supported NHC-Pd(II) catalyst to the Heck coupling reaction of a wide range of aryl halides and olefins. The results are listed in Table 5. As seen, although the palladium loading was as low as 0.25 mmol g^{-1} , excellent yields and turnover frequencies (TOFs) were obtained for the examined aryl iodides and bromides (entries 1 to 13). Meantime, the utilized aryl chlorides demonstrated a quite low reactivity under the optimal reaction conditions (entries 14 and 15). Therefore, the catalyst can efficiently promote the coupling reaction of aryl iodides and bromides with various olefins.

A possible mechanism for the Heck cross-coupling reaction catalysed by the NHC–Pd(II) complex can be proposed, as shown in Scheme 2. The mechanism is suggested based on the mechanism described by Shaw,^[55,56] in which a Pd(II)/Pd(IV) cycle is involved for pincer-type Pd(II) complexes. According to the proposed mechanism, following the coordination of olefin to the supported Pd(II), the nucleophile (KCO₃⁻) attacks the alkene-coordinated complex to give an alkyl σ -complex. The aryl halide oxidizes the Pd(II) centre, the attached nucleophile is released and the alkene coordinates to the Pd(IV) complex again. Then, the

subsequent migration, β -hydride elimination and baseinduced removal of hydrogen halide give the desired product and regenerate the catalyst.

In Table 6, the catalytic activity of the supported NHC–Pd(II) complex in the Heck cross-coupling reaction of iodobenzene with styrene is compared with that of a few catalysts reported in the literature. As seen, the as-prepared supported catalyst is more effective than the other catalysts for the studied reaction $(Q_{\rm m} = 6.02 \text{ mg g}^{-1})$. Magnetic separation is another advantage of the as-prepared supported catalyst.

3.2.2 | Recyclability of catalyst

Complicated and expensive routes are usually applied for preparing supported catalysts. Therefore, sufficient attention must be paid to the retrieval of the used catalyst from a economic point of view. In the present work, the stability and reusability of the supported NHC-Pd(II) complex were also investigated in the Heck cross-coupling reaction of iodobenzene and styrene, as model substrates, under the optimal conditions. It was observed that the reaction conversion reaches 90% during 1.0 h and gradually increases to 96% within 1.5 h in the first run. In order to regenerate the catalyst, after each cycle, the catalyst was recovered easily by simple magnetic decantation, washed with diethyl ether and dried in vacuum. As can be seen in Figure 11, the supported catalyst can be reused at least five times with no significant loss of catalytic activity. This experiment revealed that the synthesized composite is not only a highly active catalyst but it is also a stable and recyclable material under the described reaction conditions.



SCHEME 2 Proposed Pd(II)/Pd(IV) catalytic cycle for the Heck cross-coupling reaction in the presence of the supported NHC-Pd(II) complex

TABLE 6 Comparison of prepared catalyst with other catalysts for Heck cross-coupling reactions of iodobenzene with styrene

Entry	Catalyst	Conditions	Time (h)	Yield (%)	TON/TOF (h ⁻¹)	Ref.
1	Agarose-Pd(0)	Solvent-free, Et ₃ N, 100–120°C	2	90	174/87	[57]
2	PdNP-SβCD	H ₂ O, K ₂ CO ₃ , 100°C	2	99	182/91	[58]
3	Palladacycle	DMA, Et ₃ N, 140°C	18	100	504/28	[59]
4	Pd/C particles	H ₂ O, Et ₃ N, 100°C	24	23	5.76/0.24	[60]
5	Pd-MPTA-1	H ₂ O, Cs ₂ CO ₃ , 100°C	6	92	1302/217	[61]
6	Pd (OAc) ₂ (ligand-free)	PEG-400, CH ₃ COONa, 80°C	1.5	93	93/62	[62]
7	1'-Carbopalladated complexes	Et ₃ N, DMA, 80°C	3	80	159/53	[63]
8	Supported NHC-Pd(II) complex	NMP, K ₂ CO ₃ , 120°C	2	96	384/192	This work



FIGURE 11 Recycling of supported NHC–Pd(II) complex for Heck crosscoupling reaction of iodobenzene and styrene. Reaction conditions: iodobenzene (1.0 mmol), styrene (1.0 mmol), solvent (1 ml), base (1.2 mmol) and reaction time 1.5 h

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4 | CONCLUSIONS

In summary, a highly efficient and retrievable NHC– Pd(II) catalyst supported on Fe_3O_4 @SiO₂-SBA was synthesized. The obtained magnetic supported catalyst was fully characterized using FT-IR, TGA, SEM, TEM, XRD, EDX, BET, VSM and XPS analyses and it was successfully used for the Heck cross-coupling reaction of aryl halides and olefins. In addition, the catalyst was found to be effective in the Heck cross-coupling reactions of a series of substituted aryl halides and olefins, as it provided excellent yields. The applied catalyst could be easily retrieved from the reaction mixture through magnetic separation and re-used for at least five consecutive cycles.

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