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Palladium nanoparticles immobilized on magnetic nanoparticles: An efficient semi-heterogeneous catalyst for carbonylation of aryl bromides

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ABSTRACT

We describe a method for supporting palladium nanoparticles on magnetic nanoparticles modified with amino-functionalized dihydro-imidazolium groups. This catalytic system is very efficient in alkoxy- and amino-carbonylation reactions of aryl bromides. The catalyst can be easily recovered from the reaction mixture by applying an external magnetic field and reused for over five consecutive cycles without a significant decrease in its activity.

1. Introduction

Transition metal catalyzed carbonylation reactions, in particular, alkoxy- and amino-carbonylation are considered as one of highly efficient protocols for the synthesis of aryl carbonyl compounds [1–3]. These reactions have attracted numerous attentions and are widely acknowledged as an essential tool in organic and industrial chemistry, in which valuable building blocks for pharmaceutical, agrochemical and biologically active compounds are synthesized [4–7]. In addition, carbonylation reactions are alternative methods for the traditional esterification and amidation reactions since it endures an ample scope of substrates [8–11]. Alkoxy- and amino-carbonylation reactions are direct and constructive approaches for the synthesis of amides and esters via coupling of aryl halides with an appropriate alcohols and amines. In this context, various palladium based catalysts, such as $PdCl_2(PPh_3)_2$/$PdBr_2(PPh_3)_2$ [12], $PdCl_2(PhCN)_2$ [13], $Pd(OAc)_2/PPh_3$ [14,15], and $Pd(dppp)Cl_2$ [16] have been utilized in the carbonylation reactions under homogeneous conditions [17,18]. Although these catalytic systems exhibited high catalytic activity, their recovery from the reaction mixture and reusability is challenging. Moreover, the removal of the palladium and the toxic phosphine residues from the final product is very complicated and uneconomic process, which makes the homogeneous catalysts inapplicable especially for large-scale production. To overcome these inherent drawbacks, several methodologies and strategies for heterogenization of phosphine free catalysts have been developed. In this regard, silica [19], zeolite [20], carbon [21] and polymer [22] supports were explored in the carbonylation reactions. Nevertheless, these heterogeneous catalytic systems still demand time consuming and tedious procedures such as centrifugation and filtration for their recovery. Hence, the development of alternative and easily separable heterogeneous catalysts while maintaining high accessibility and catalytic activity is extremely desirable. Magnetic isolation based technique is considered as a convenient strategy which meets these requirements [23].

Magnetic nanoparticles (MNPs), with their intrinsic high surface area, superparamagnetic properties, high stability and reactivity and facile preparation have emerged as a robust heterogeneous catalyst supports which could be instantaneously isolated simply by applying an external magnetic field [24–27]. However, bare MNPs tend to agglomerate within a short period of time. Avoiding this restriction could be achieved by applying a surface coating and capping methods using organic/inorganic polymers and small capping agents like silane reagents [28–34]. Apart from preventing the undesirable coagulations, various functionalities could be simultaneously introduced to the catalyst support.

To the best of our knowledge, magnetically retrievable palladium based nanocatalyst has not been explored in the alkoxycarbonylation and aminocarbonylation reactions. Herein, we report a facile synthesis of phosphine free supported palladium nanoparticles on the surface of MNPs modified with amino-functionalized ionic liquid (IL) groups as a robust, efficient and easily recyclable semi-heterogeneous catalyst for the alkoxy- and amino-carbonylation reactions of aryl bromides. These ionic liquid groups are competent of tuning and enhancing the dispersibility of the magnetic support and the immobilized catalyst in various polar organic and aqueous solvents. In addition, the presence

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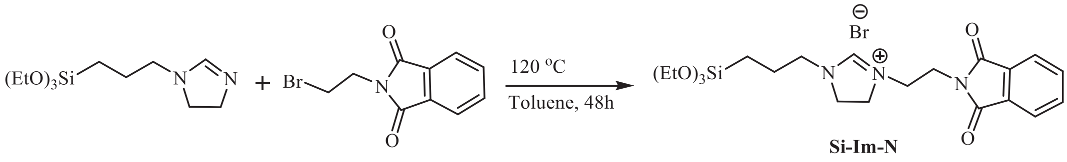


Scheme 1. Synthesis of 3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1-(3-(triethoxysilyl)propyl)-4,5-dihydro-1H-imidazol-3-ium bromide.

of the amine functionality highly contributes to the immobilization and stabilization of the catalytically active palladium nanoparticles.

2. Experimental

2.1. Characterization

Transmission electron microscope (TEM) and electron diffraction spectroscopy (EDS) were performed with (S) TEM Tecnai F20 G2 (FEI Company, USA) operated at 200 kV. The infrared spectra were recorded at room temperature in transmission mode using a Perkin Elmer spectrometer 65 FTIR. Thermogravimetric analysis (TGA) was performed on Mettler Toledo TG 50 analyzer. Measurements were carried out at temperature range that extended from 25–950 °C at a heating rate of 10 °C/min under air. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker DRX-400 or 500 MHz instrument in $CDCl_3$. Inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed on 7500cx (Agilent company) using an external standard calibration. Powder X-ray diffraction (XRD) measurements were performed on the D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with a goniometer radius 217.5 mm secondary graphite mono-chromator, 2° Soller slits and 0.2 mm receiving slit. Low-background quartz sample holders were carefully filled with the powder samples. XRD patterns within the range 1° to 75° 2θ were recorded at room temperature using CuKα radiation ($\lambda = 1.5418$ Å) with the following measurement conditions: tube voltage of 40 kV, tube current of 40 mA, step-scan mode with a step size of 0.02° 2θ and counting time of 1 s/step. The X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Axis Ultra X-ray photoelectron spectrometer (Kratos Analytical Ltd., Manchester, UK) using an Al Kα monochromatic radiation source (1486.7 eV) with 90° takeoff angle (normal to analyzer).

2.2. Synthesis of 3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1-(3-(triethoxysilyl)propyl)-4,5-dihydro-1H-imidazol-3-ium bromide (Si-Im-N)

A mixture of N-(2-bromoethyl)phthalimide (5.06 g, 20 mmol) and N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole (5.5 g, 20 mmol) in 60 mL dry toluene was stirred under inert atmosphere at 120 °C for 48 h. The mixture was cooled down to room temperature, and the solvent was removed under vacuum in a rotary evaporator resulting in a brown viscous liquid. The product was washed with diethyl ether (3 × 50 mL) to afford an off-white hygroscopic solid in 91% yield (9.5 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.54 (t, $J = 8$ Hz, 2H),1.2 (t, $J = 4.4$ Hz, 9H), 1.67–1.74 (m, 2H), 3.56 (t, $J = 7.6$ Hz, 2H), 3.79 (q, $J = 7.2$ Hz, 6H), 3.92–4.06 (m, 6H), 4.19 (t, $J = 9.2$ Hz, 2H), 7.73 (dd, $J = 3.2$, 2.8 Hz, 2H), 7.85 (dd, $J = 3.2$, 2.8 Hz, 2H), and 9.41 (s, 1H); ^{13}C NMR (100 MHz, CDCl3) δ (ppm): 6.91, 18.29, 21.00, 35.22, 47.62, 48.39, 48.50, 50.52, 56.99, 58.50, 123.64, 131.67, 134.40, 158.63, and 168.16. Elemental anal. for $C_{22}H_{34}BrN_3O_5Si$. Calculated: C 50.00, H 6.48, N 7.95; Found: C 50.80, H 6.52, N 7.90.

2.3. General procedure for the modification of magnetic nanoparticles with the dihydro-imidazolium groups (MNP-Im-N)

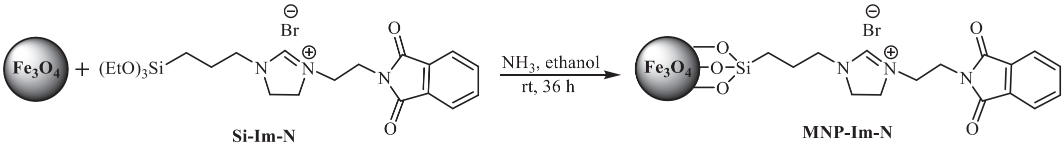
The magnetite nanoparticles were prepared according to Massart's method [35]. 11.7 g $FeCl_3 \cdot 6H_2O$ and 4.4 g $FeCl_2 \cdot 4H_2O$ was dissolved and mechanically stirred in 400 mL deionized water under inert atmosphere. The mixture was heated at 85 °C followed by quick addition of 18 mL concentrated ammonia (25%) generating a black suspension of magnetite nanoparticles. The mixture was heated for further 30 min, and then it was allowed to cool to room temperature. The black magnetite nanoparticles were separated via external magnetic force and washed 5 times with 200 mL deionized water. The magnetic nanoparticles were suspended in 500 mL ethanol and sonicated for 60 min. The resulted black suspension was mechanically stirred and a 100 mL ethanol solution containing the monomer Si-Im-N (5.29 g, 10 mmol) and 15 mL concentrated ammonia (25%) were added and the reaction mixture was allowed to stir under nitrogen for 36 h at room temperature. The resulted modified nanoparticles were magnetically separated and washed with ethanol (4 × 50 mL). Finally, they were suspended in 300 mL of ethanol and sonicated for another 60 min.

2.4. Supporting palladium nanoparticles on the modified magnetic nanoparticles (MNP-Im-NH_2-Pd)

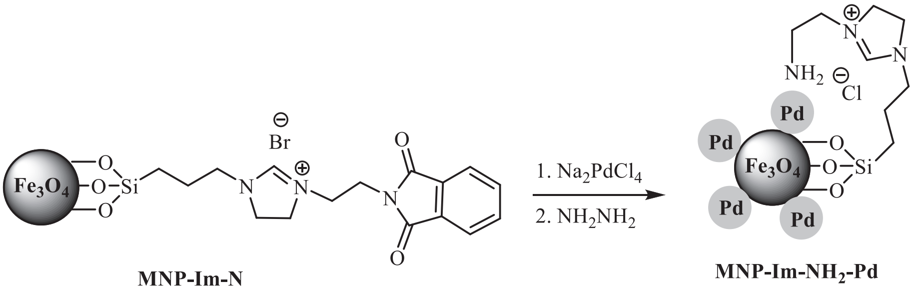
A suspension of 100 mL of the modified magnetic nanoparticles in ethanol was sonicated for 30 min followed by the addition of Na_2PdCl_4 (150 mg, 0.43 mmol) dissolved in 10 mL of deionized water. The reaction mixture was mechanically stirred for 24 h, and then 6 mL hydrazine hydrate was added. The reaction mixture was allowed to stir for further 5 h. The supported palladium nanoparticles were magnetically separated, washed with methanol (2 × 100 mL) and eventually suspended in 200 mL methanol. The loading of the palladium in the system is 0.16 mmol g^{-1} as determined by ICP–MS analysis.

2.5. General procedure for the alkoxycarbonylation reaction of bromoarenes

A 25 mL glass lined autoclave was charged with bromoarene (4 mmol), triethylamine (8 mmol) and MNP-Im-NH_2-Pd (0.02 mmol Pd in 5 mL dry alcohol). The autoclave was sealed, purged three times with carbon monoxide (CO), and pressurized to 500 psi with CO. The reaction mixture was stirred at 130 °C for 24 h. The autoclave was cooled to room temperature and CO was carefully released. The catalytic system was magnetically separated and the solution decanted and evaporated under vacuum in a rotary evaporator. The product was diluted with ether (20 mL), washed with aqueous hydrochloric acid (2



Scheme 2. Modification of magnetite nanoparticles with Si-Im-N.



Scheme 3. Preparation of palladium nanoparticles supported on magnetite nanoparticles.

× 10 mL, 1N), dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The products were purified by column chromatography on silica gel (ethylacetate:hexane 20:1 as an eluent solvent) to afford the desired products.

2.6. General procedure for the aminocarbonylation reaction of bromoarenes

A 25 mL glass lined autoclave was charged with bromoarene (4 mmol), amine (8 mmol), triethylamine (8 mmol) and MNP-Im-NH$_2$-Pd (0.02 mmol Pd in 5 mL dry toluene). The autoclave was sealed, purged three times with carbon monoxide (CO), and pressurized with CO to 500 psi. The reaction mixture was stirred at 130 °C for 24 h. The autoclave was cooled to room temperature and CO was carefully released. The catalytic system was magnetically separated and the solution decanted evaporated under vacuum in a rotary evaporator. The product was diluted with ether (15 mL), washed with water (3 × 5 mL), dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The products were purified by column chromatography on silica gel (ethylacetate:hexane 90:10 as an eluent solvent) to afford the desired products.

3. Results and discussion

3.1. Synthesis of palladium nanoparticles supported on ionic liquid modified magnetic nanoparticles

First, the MNPs were prepared via simple co-precipitation method of iron salts, FeCl$_2$ and FeCl$_3$ in a basic aqueous solution at 85 °C according to Massart's method [35]. The resulted particles were spherical in shape with a size range of 5–20 nm. Nonetheless, an unavoidable obstacle associated with this size is that the particles are intrinsically unstable and tend to agglomerate in order to reduce their surface energy. In addition, bare MNPs are hardly dispersible in any medium. As a result, several surface modifications and protection approaches of the bare MNPs have been introduced in order to overcome the aforementioned drawbacks. It is noteworthy that in addition to the protection strategy, the MNPs can be easily functionalized with various coupling agents or functional groups. In our study, the MNPs were protected successfully via facile covalent functionalization with the silane monomer 3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1-(3-(triethoxysilyl)propyl)-4,5-dihydro-1H-imidazol-3-ium bromide. As depicted in Scheme 1, this silane monomer was synthesized by reacting N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole with *N*-(2-bromoethyl)phthalimide in dry toluene under inert atmosphere at 120 °C for 48 h. After cooling and washing, the desired silane monomer was obtained as an off-white hygroscopic solid in 90% yield.

The modification process of the MNPs was accomplished by reacting the triethoxysilane groups of the Si-Im-N with the surface hydroxyl groups of the MNPs via sol–gel condensation under basic conditions in ethanol for 36 h (Scheme 2). While the bare magnetite nanoparticles are not dispersible in organic solvents, the modified MNPs were highly dispersible in water and polar organic solvents such as methanol and ethanol.

The modified MNPs were utilized for supporting palladium nanoparticles. Initially, Na$_2$PdCl$_4$ was adsorbed via ion exchange on the surface of the MNPs by stirring the MNPs containing imidazolium units with the palladium salt in ethanol for 24 h, followed by reducing the palladium ions with hydrazine hydrate. Simultaneously; the phthalimide groups were removed by reaction with the excess of hydrazine hydrate to afford amine groups (Scheme 3). While the presence of the imidazolium groups enhances the dispersibility of the resulted material in polar organic solvents, the existence of amine groups provides coordination sites that can strengthen the immobilization of the palladium NPs on the magnetite surface. When bare MNPs were utilized as the solid support, no palladium NPs formed on the surface of the MNPs as confirmed by transmission electron microscope (TEM) and scanning transmission electron microscope/energy dispersive X-ray spectroscopy (STEM/EDS) analysis (Supporting information, Fig. S1).

The MNP-Im-NH$_2$-Pd catalyst was characterized by TEM (Fig. 1). The TEM micrographs confirmed the formation of magnetite nanoparticles with a size range of 5–20 nm in addition to the creation of palladium

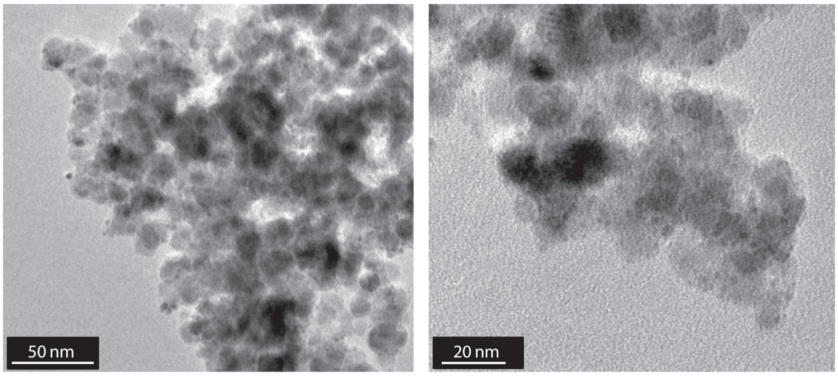


Fig. 1. TEM micrographs of palladium supported on magnetic nanoparticles modified with amino-functionalized dihydro-imidazolium groups.

nanoparticles. STEM/EDS and X-ray photoelectron spectroscopy (XPS) analyses also indicated the presence of the palladium nanoparticles on the surface of the modified magnetite nanoparticles (Supporting information, Fig. S2 and S3, respectively). In the XPS spectrum, the binding energy of MNP-Im-NH_2-Pd system exhibits two strong characteristic peaks at 334.9 eV and 340.1 eV, which are ascribed to Pd $3d_{5/2}$ and Pd $3d_{3/2}$, respectively (Supporting information, Fig. S3).

The catalytic system was further analyzed by powder X-ray diffraction (XRD). The XRD pattern displayed the characteristic peaks of MNPs at $2\theta = 18.3, 30.1, 35.5, 43.3, 53.5, 57.1, 62.6, 71$ and 74 with a cubic unit cell (Fig. 2a). Additionally, it shows the characteristic peaks of the palladium nanoparticles at $2\theta = 40, 46.6$ and 67.5 which match well with the characteristic peaks of fcc palladium crystal structure (Fig. 2b). These peaks are attributed to (100), (200) and (220) reflections, respectively. According to Scherrer equation the average crystallite size of the palladium nanoparticles is 7.04 nm.

Further characterization was conducted by thermal gravimetric analysis (TGA) to study the thermal decomposition of the bare MNPs, MNP-Im-N and MNP-Im-NH_2-Pd systems. The thermal decomposition analysis was carried out in the temperature range of 25–950 °C under air. This analysis showed an increase in the organic content after functionalizing the MNPs with the silane monomer Si-Im-N with a 21% weight loss (Fig. 3c) compared to the bare magnetite nanoparticles with weight loss of 3% (Fig. 3a), which belongs to solvent residues. Whereas, the MNP-Im-NH_2-Pd system exhibited weight loss of 18% indicating a lower percentage of organic content due to the removal of the phthalimide protecting group by hydrazine hydrate (Fig. 3b).

The removal of the phthalimide group was also confirmed by infrared analysis (Fig. 4). The disappearance of the C═O stretching vibration peak at 1710 cm^{-1} and C–N (of the imide groups) peak at 1398 cm^{-1} in MNP-Im-NH_2-Pd (Fig. 4a), substantiates that the phthalimide groups were disconnected successfully during the reduction of the palladium salts with hydrazine hydrate.

3.2. Catalysis

The catalytic efficiency of the MNP-Im-NH_2-Pd system was appraised in two types of carbonylation reactions of aryl bromides: Alkoxycarbonylation and aminocarbonylation. The alkoxycarbonylation reactions were conducted with 0.5 mol% MNP-Im-NH_2-Pd in dry methanol at 130 °C under a constant CO pressure of 500 psi. Initially, the influence of the base type applied in these reactions was investigated using bromobenzene and methanol as substrates. When inorganic bases such as K_2CO_3 and Cs_2CO_3 were utilized, methyl benzoate was obtained in a yield of 80% and 75%, respectively. However, the yield of the desired product was increased to 90% when Et_3N was employed.

The scope of the nanocatalyst MNP-Im-NH_2-Pd in the alkoxycarbonylation was further extended to a various aryl bromides and diverse alcohols. The results are presented in Table 1. Bromobenzene reacted efficiently with various alcohols such as methanol, ethanol and benzyl alcohol providing the corresponding products in high yields (Table 1, entries 1, 5 and 6). The methoxycarbonylation of the substituted bromobenzene derivatives, 4-bromoanisole, 4-bromoacetophenone and 4-bromotoluene afforded the proper ester in a yield of 90%, 92% and 90% (Table 1, entries 2–4), respectively. These results show that the presence of electron-donating and electron-withdrawing groups has an insignificant effect on the catalytic efficiency.

Furthermore, the reactivity of the nanocatalyst MNP-Im-NH_2-Pd was investigated in the carbonylation reaction of bromobenzene with phenol in the presence of Et_3N and 500 psi CO at 130 °C (Table 1, entry 7). This reaction was conducted in various solvents such as toluene, water, DMF and dioxane affording 85%, 0%, 50% and 60% yields, respectively. Under the same reaction condition and with toluene as a solvent, 4-bromoacetophenone reacted with phenol to provide the corresponding ester product in a yield of 86% (Table 1, entry 8). The nanocatalyst MNP-Im-NH_2-Pd was further applied in the aminocarbonylation reaction of aryl bromides with various amines. First, a reaction of bromobenzene and aniline was conducted with 0.5 mol% MNP-Im-NH_2-Pd in toluene under 500 psi CO at 130 °C for 24 h. 86% of the desired amide product was obtained (Table 2, entry 1). However, when other solvents such as DMF and water were used in the same reaction, the yield was decreased to 75% and 70%, respectively.

Under the aforementioned reaction conditions, carbonylation reaction of different aromatic and aliphatic amines with aryl bromides was investigated (Table 2). The reaction of cyclohexylamine and

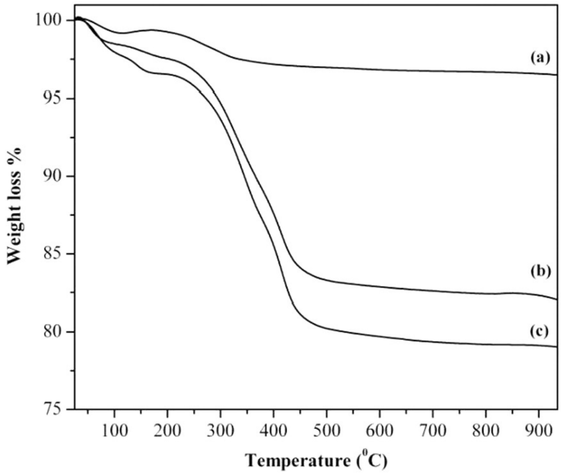


Fig. 3. TGA curves of a) bare MNPs; b) MNP-Im-NH_2-Pd and c) MNP-Im-N.

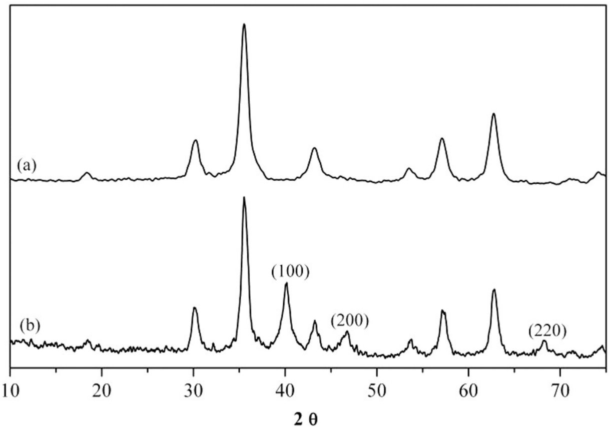


Fig. 2. XRD pattern of a) bare MNPs and b) MNP-Im-NH_2-Pd.

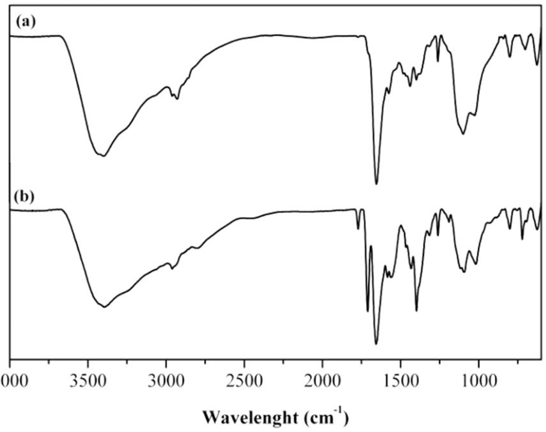
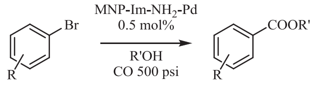
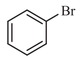
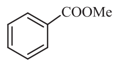
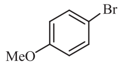
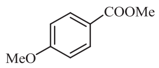
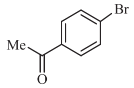
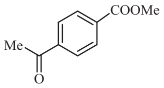
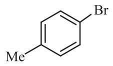
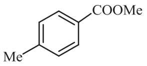
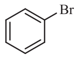
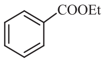
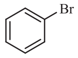
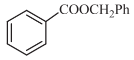
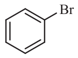
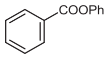
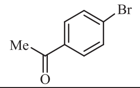
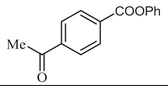


Fig. 4. Transmission FTIR spectra of a) MNP-Im-NH_2-Pd and b) MNP-Im-N.

Table 1
Alkoxycarbonylation reactions of aryl bromides with various alcohols catalyzed by MNP-Im-NH_2-Pd[a].



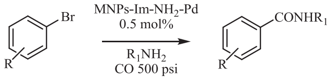
Entry	Arylbromide	Alcohol	Product	Yield[b]
1		MeOH		90
2		MeOH		90
3		MeOH		92
4		MeOH		90
5		EtOH		95
6		$PhCH_2OH$		85
7[c]		PhOH		85
8[c]		PhOH		86

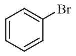
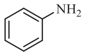
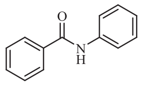
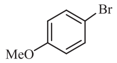
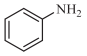
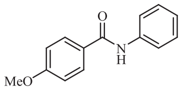
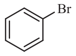
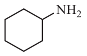
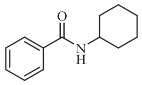
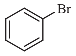
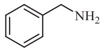
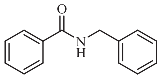
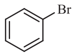
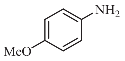
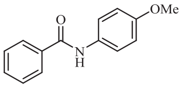
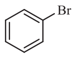
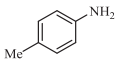
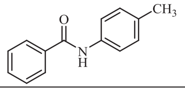
[a] Reaction conditions: 4 mmol aryl bromide, 5 mL alcohol, 0.5 mol% MNP-Im-NH_2-Pd, 8 mmol Et_3N, 500 psi CO, 24 h at 130 °C.

[b] Isolated yield.

[c] 4 mmol phenol, 5 mL toluene.

Table 2
Aminocarbonylation reactions of aryl bromides with various amines catalyzed by MNP-Im-NH_2-Pd[a].



Entry	Arylbromide	amine	Product	Yield[b]
1				86
2				80
3				84
4				80
5				79
6				75

[a] Reaction conditions: 4 mmol aryl bromide, 8 mmol amine, 0.5 mol% MNP-Im-NH_2-Pd, 8 mmol Et_3N, 500 psi CO, 24 h at 130 °C, 10 mL toluene.
[b] Isolated yield.

benzylamine with bromobenzene afforded the desired amide product in 84% and 80% yields, respectively (Table 2, entries 3 and 4), whereas 4-bromoanisole with aniline provided an 80% yield (Table 2, entry 2). Furthermore, substituted amines such as 4-methoxyaniline and 4-methylaniline underwent aminocarbonylation reaction with bromobenzene to afford 79% and 75% yields of the amide products (Table 2, entries 5–6), respectively.

3.2.1. Recyclability of MNP-Im-NH_2-Pd

Recovery and reuse of the heterogeneous catalysts is one of the major concerns due to the perspectives of green chemistry. The recyclability of the nanocatalyst MNP-Im-NH_2-Pd was assessed in the methoxycarbonylation reaction of bromobenzene with methanol. Due to the magnetic properties of MNP-Im-NH_2-Pd, the catalyst was easily separated from the reaction mixture simply by applying an external magnetic field and recycled over 5 times without observing any significant loss in its catalytic activity (Fig. 5). In addition, ICP–MS analysis was utilized to examine if there was a leaching of palladium species to the reaction medium. This analysis revealed that 1.3 ppm of palladium exists in the solvent after methoxycarbonylation of bromobenzene. However, this result indicates that the leaching extent of the palladium species from the magnetic nanosupport is negligible.

4. Conclusion

In this work, we have developed magnetically retrievable semi-heterogeneous catalytic system for the alkoxycarbonylation and aminocarbonylation reactions of aryl bromides. This catalytic system is based on supporting palladium nanoparticles on magnetite nanoparticles modified with amino-functionalized dihydro-imidazolium groups. The modification of the magnetic nanoparticles with these groups was carried out to enhance the dispersibility of the magnetic nanosupports in polar organic solvents and stabilize the immobilized palladium nanoparticles via coordination with the amine groups. The nanocatalyst developed in our study could be isolated easily by applying an external magnetic field and recycled five times without a significant decrease in its reactivity.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.12.001.

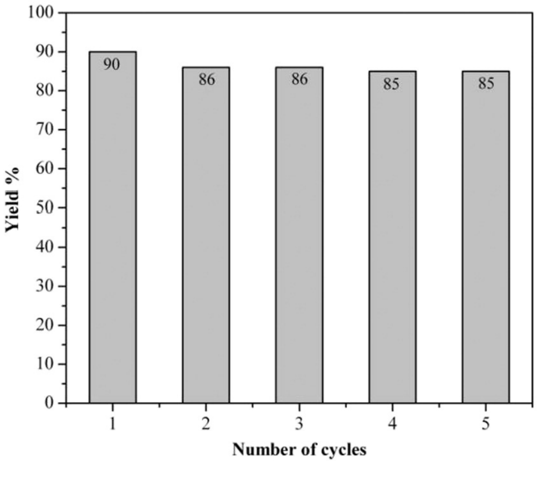


Fig. 5. Recyclability of MNP-Im-NH_2-Pd nanocatalyst in the methoxycarbonylation of bromobenzene.

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