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Pd(0)-Arg-boehmite: As Reusable and Efficient Nanocatalyst in Suzuki and Heck Reactions

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Abstract The direct supporting of Pd-arginine complex on boehmite nanoparticles (Pd(0)-Arg-boehmite) was reported as a moisture- and air-stable, heterogeneous, excellent and novel organometallic catalyst, which applied for the Suzuki and Heck cross coupling reactions through coupling of phenylboronic acid, 3,4-difluoro phenylboronic acid, sodium tetraphenyl borate, butyl acrylate, methyl acrylate, acrylonitrile and styrene with a wide range of aryl halide including Cl, Br and I. Pd(0)-Arg-boehmite was prepared for the first time via simple, environmental and inexpensive procedure in water and ethanol without inert atmosphere or high temperature using commercially available materials, and characterized by XRD, TGA, TEM, SEM, EDS and ICP-OES techniques. The leaching of palladium and heterogeneity test of this catalyst was studied by hot filtration and ICP-OES techniques; resulting we found that this catalyst was demonstrated remarkable and excellent recyclability.

Graphical Abstract Boehmite nanoparticles were prepared by inexpensive procedure in water at room temperature and directly immobilized with a new type of Pd-arginine complex. After characterization of this catalyst, its application has been studied for the C–C coupling reactions.

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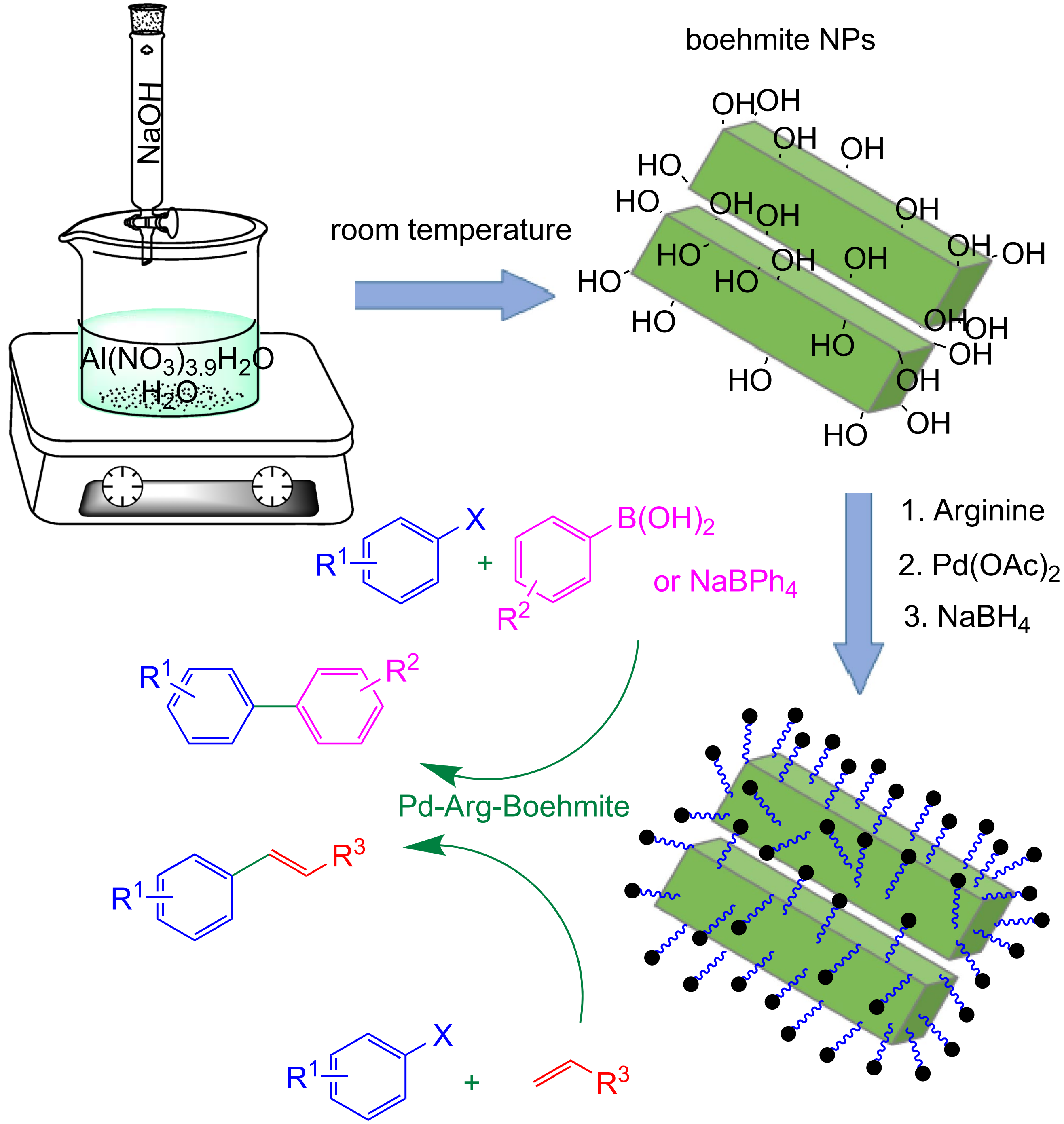


Keywords Boehmite nanoparticles · Arginine · Palladium · Suzuki reaction · Heck reaction · C–C coupling

1 Introduction

Carbon–carbon coupling reactions are commonly have been catalyzed by homogeneous or heterogeneous Pd-complexes [1–4] and were used as a powerful tools in modern synthetic organic chemistry for the preparation of natural products, advanced materials, polymers, pharmaceuticals, agrochemicals, biologically active compounds, herbicides, UV screens and liquid crystal materials [5–8]. For this aim, many methods including variety homogeneous or heterogeneous catalysts have been developed over the years to find efficient C–C bond formation such as Suzuki and Heck reactions. However, in order to perform facile catalyst recovery and excellent reusability of catalysts;

immobilization of homogeneous catalysts on insoluble supports have been widely employed as useful and efficient procedure in organic synthesis [9, 10]. In order to combine the advantages of both homogeneous (high catalytic activity) and heterogeneous (easily recyclable, moisture and air stable) catalysts, nanoparticles (NPs) have been recently emerged as great and useful heterogeneous supports for the immobilization of homogeneous catalysts [11, 12]. However, many supports such as MCM-41 [13], SBA-15 [14] or some nanoparticles such as TiO_2 NPs [15] and iron oxide [16, 17] have been employed for the catalyst supports, which requires high temperature for calcination or inert atmosphere and a lot of time and tedious condition to prepare. Also, most of previously heterogeneous supports such as carbon nanotubes [18], heteropolyacids [19], molecular sieve [20], ionic liquids [21, 22], graphene oxide [23] or some polymers [24] are cost effective. While preparation of boehmite nanoparticles was not air or moisture sensitive, more important boehmite nanoparticles was prepared in water at room temperature without inert atmosphere using commercial materials such as $Al(NO_3)_3 \cdot 9H_2O$ and NaOH [25]. Boehmite nanoparticles are an orthorhombic structure of aluminum oxide hydroxide (γ-AlOOH) [26]. Although nanoboehmite has large specific surface area (>120 m^2/g) [27] and high thermal, chemical and mechanical stability [28, 29], but nanoboehmite is rarely used as heterogeneous support for the immobilization of homogeneous catalysts [27, 28, 30]. Therefore owing to the context of reuse of palladium, herein Pd-arginine complex on boehmite nanoparticles as a novel nano heterogeneous catalyst has been reported for C–C coupling reactions.

2 Experimental

2.1 Materials

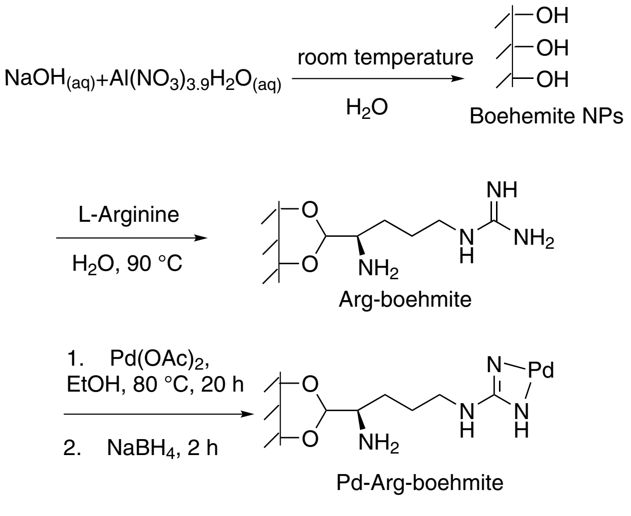
Chemicals and solvents used in this work were obtained from Sigma-Aldrich, Fluka or Merck chemical companies and used without further purification. Boehmite nanoparticles and Pd-SMTU-boehmite were identified using a Holland Philips X'pert X-ray powder diffraction (XRD) diffractometer, at a scanning speed of 2° per minute from 2° to 80°. Thermogravimetric analyses (TGA) of the samples were recorded using a Shimadzu PL-STA 1500 device in the temperature range 30–800 °C. The particle size and morphology were examined by measuring SEM using FESEM-TESCAN MIRA3, on an accelerating voltage of 30.0 kV and also using Zeiss-EM10C transmission electron microscope (TEM). The content of Pd was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES). NMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 MHz. Melting points were measured with an Electrothermal 9100 apparatus.

2.2 Preparation of Catalyst (Pd(0)-Arg-boehmite)

The solutions of NaOH (6.490 g) in 50 mL of distilled water was added to solutions of $Al(NO_3)_3 \cdot 9H_2O$ (20 g) in 30 mL distilled water as drop to drop under vigorous stirring. The resulting milky mixture was subjected to mix in the ultrasonic bath for 3 h at 25 °C. The resulted nano aluminum oxihydroxide was filtered and washed by distilled water and were kept in the oven at 220 °C for 4 h. The obtained boehmite nanoparticles (1.5 g) were dispersed in 50 mL deionized water, and then 2.5 mmol of L-Arginine was added to the mixture. The reaction mixture was stirred at 90 °C for 24 h. Then, the prepared nanoparticles (Arg@boehmite) was filtered, washed with ethanol and dried at room temperature. The obtained Arg@boehmite (0.5 g) was dispersed in 25 mL ethanol, and then palladium acetate (0.25 g) was added to the reaction mixture. The reaction mixture was stirred at 80 °C for 20 h. Then, the $NaBH_4$ (0.3 mmol) was added to the reaction mixture and was allowed to run for another 2 h. The final product (Pd-Arg@boehmite) was filtered, washed by ethanol and dried at room temperature.

2.3 General Procedure for the Suzuki Reaction

A mixture of aryl halide (1 mmol), boronic compound (0.5–1 mmol), Na_2CO_3 (3 mmol), and Pd(0)-Arg-boehmite (0.008 g, 1.08 mol%) were added to a reaction vessel. The resulting mixture was stirred in PEG at 80 °C and



Scheme 1 Synthesis of Pd(0)-Arg-boehmite

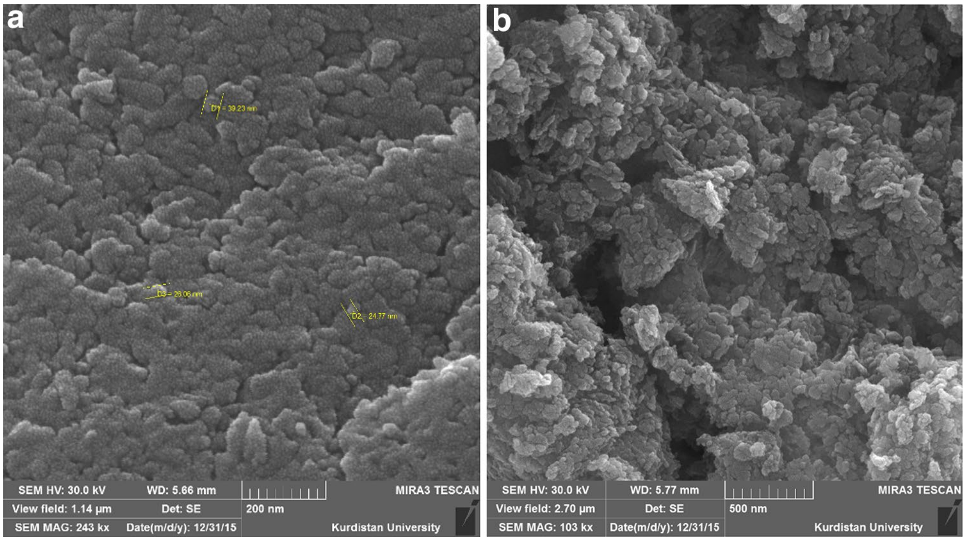


Fig. 1 SEM images of boehmite nanoparticles (**a**) and Pd(0)-Arg-boehmite (**b**)

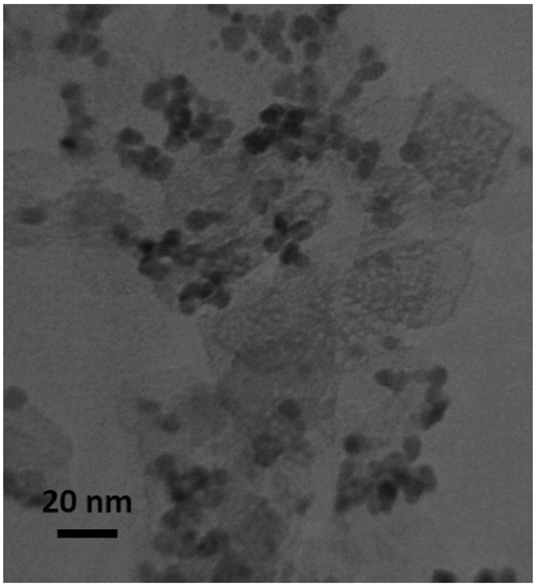


Fig. 2 TEM image of Pd(0)-Arg-boehmite

the progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated and washed with ethylacetate and the reaction mixture was extracted with H_2O and ethylacetate and dried over anhydrous Na_2SO_4 (1.5 g). Then the solvent was evaporated and pure biphenyl derivatives were obtained in good to excellent yields.

2.4 General Procedure for the Heck Reaction

A mixture of aryl halide (1 mmol), alkene (1.2 mmol), Na_2CO_3 (3 mmol), and Pd(0)-Arg-boehmite (0.016–0.02 g, 2.16–2.7 mol%) was stirred in DMF at 120 °C and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and catalyst was separated and washed with diethyl ether and the reaction mixture was extracted with H_2O and diethyl ether. The organic layer was dried over Na_2SO_4 (1.5 g). Then the solvent was evaporated and pure products were obtained in good yields.

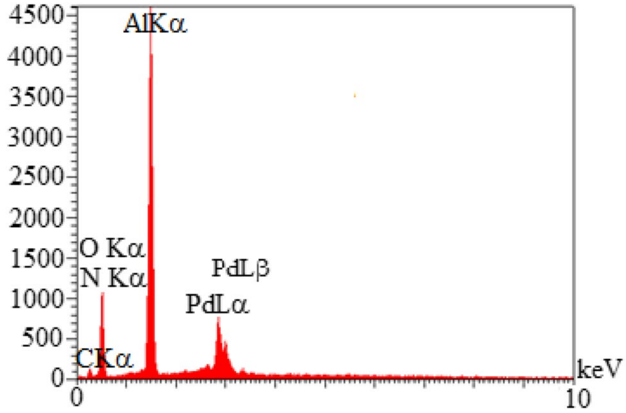


Fig. 3 EDX spectrum of Pd(0)-Arg-boehmite

2.5 Selected Spectral Data

2.5.1 *1,1′-Biphenyl*

^{1}H NMR (400 MHz, $CDCl_3$): $\delta_H = 7.65–7.63$ (m, 4H), 7.51–7.41 (m, 4H), 7.41–7.37 (tt, $J = 7.6$, 1.2 Hz, 2H) ppm.

2.5.2 *4-Chloro-1,1′-biphenyl*

^{1}H NMR (400 MHz, $CDCl_3$): $\delta_H = 7.60–7.58$ (m, 2H), 7.57–7.54 (m, 2H), 7.50–7.43 (m, 4H), 7.42–7.38 (tt, $J = 6$, 1.6 Hz, 1H) ppm.

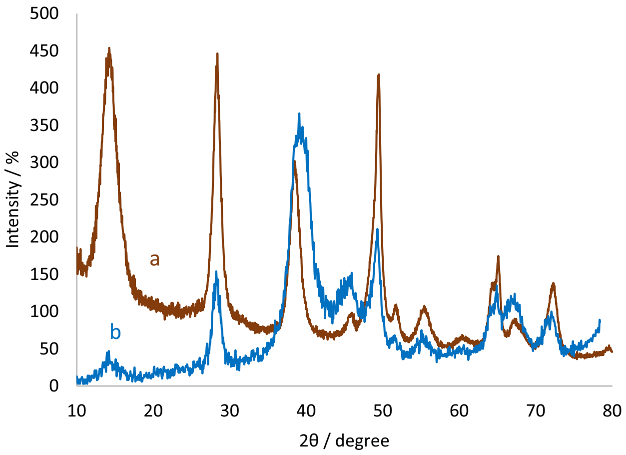


Fig. 4 The XRD patterns of boehmite nanoparticles (**a**) and Pd(0)-Arg-boehmite (**b**)

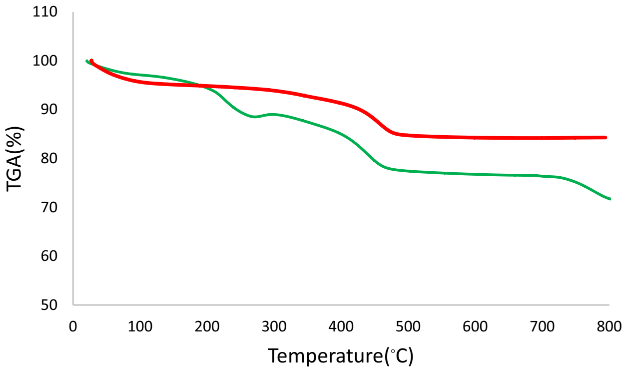


Fig. 5 TGA diagram of boehmite (*red line*) and Pd(0)-Arg-boehmite (*green line*)

2.5.3 3,4-Difluoro-1,1'-biphenyl

^{1}H NMR (400 MHz, CDCl$_3$): δ_H = 7.81–7.75 (m, 1H), 7.71–7.69 (m, 2H), 7.57–7.53 (m, 2H), 7.51–7.46 (m, 2H), 7.43–7.39 (m, 1H) ppm.

2.5.4 Butyl cinnamate

^{1}H NMR (400 MHz, CDCl$_3$): δ_H = 7.74–7.70 (d, J = 16 Hz, 1H), 7.57–7.55 (m, 2H), 7.43–7.40 (m, 3H), 6.50–6.46 (d, J = 16 Hz, 1H), 4.26–4.23 (t, J = 6.4 Hz, 2H), 1.76–1.70 (m, 2H), 1.50–1.45 (m, 2H), 1.02–0.98 (t, J = 7.6 Hz, 3H) ppm.

2.5.5 Butyl 3-(4-methoxyphenyl)acrylate

^{1}H NMR (400 MHz, CDCl$_3$): δ_H = 7.68–7.64 (d, J = 15.6 Hz, 1H), 7.51–7.49 (d, J = 6.8 Hz, 2H), 6.93–6.92 (d, J = 7.2 Hz, 2H), 6.36–6.32 (d, J = 16 Hz, 1H), 4.24–4.21 (t, J = 6.4 Hz, 2H), 3.85 (s, 3H), 1.73–1.67 (quint, J = 6.8 Hz, 2H), 1.51–1.42 (sixt, J = 8 Hz, 2H), 1.01–0.97 (t, J = 7.6 Hz, 3H) ppm.

2.5.6 1,2-Diphenylethene

^{1}H NMR (400 MHz, CDCl$_3$): δ_H = 7.58–7.56 (d, J = 7.6 Hz, 4H), 7.43–7.39 (t, J = 7.6 Hz, 4H), 7.33–7.29 (m, 2H), 7.16 (s, 2H) ppm.

2.5.7 1-Methyl-4-styrylbenzene

^{1}H NMR (400 MHz, CDCl$_3$): δ_H = 7.56–7.54 (d, J = 7.6 Hz, 2H), 7.47–7.45 (d, J = 8 Hz, 2H), 7.41–7.37 (t, J = 7.2 Hz, 2H), 7.30–7.28 (t, J = 4 Hz, 1H), 7.22–7.20 (d, J = 8 Hz, 2H), 7.12–711 (d, J = 2.4 Hz, 2H), 2.40 (s, 3H) ppm.

2.5.8 3-(p-Tolyl)acrylonitrile

^{1}H NMR (400 MHz, CDCl$_3$): δ_H = 7.42–7.37 (m, 3 H), 7.29–7.23 (m, 2 H), 5.88–5.84 (d, J = 16.4 Hz, 1 H), 2.42 (s, 3 H) ppm.

3 Result and Discussion

3.1 Catalyst Preparation

The Pd(0)-Arg-boehmite was prepared according to the concise route outlined in Scheme 1. Initially boehmite nanoparticles has been synthesized by addition of sodium hydroxide to the aqueous solution of aluminum nitrate as aluminum source, at room temperature and subsequently Pd-arginine complex was supported on surface of prepared particles, directly.

3.2 Catalyst Characterizations

This catalyst has been characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and inductively coupled plasma atomic emission spectroscopy (ICP-OES).

The SEM images of boehmite nanoparticles and Pd(0)-Arg-boehmite are shown in Fig. 1. As shown in these images, the size and morphology of boehmite and Pd(0)-Arg-boehmite are quite homogeneous particles in the range of 20–25 nm. SEM images of boehmite and catalyst are in good agreement with each other in terms of size and shape. Also, TEM image of catalyst (Fig. 2)

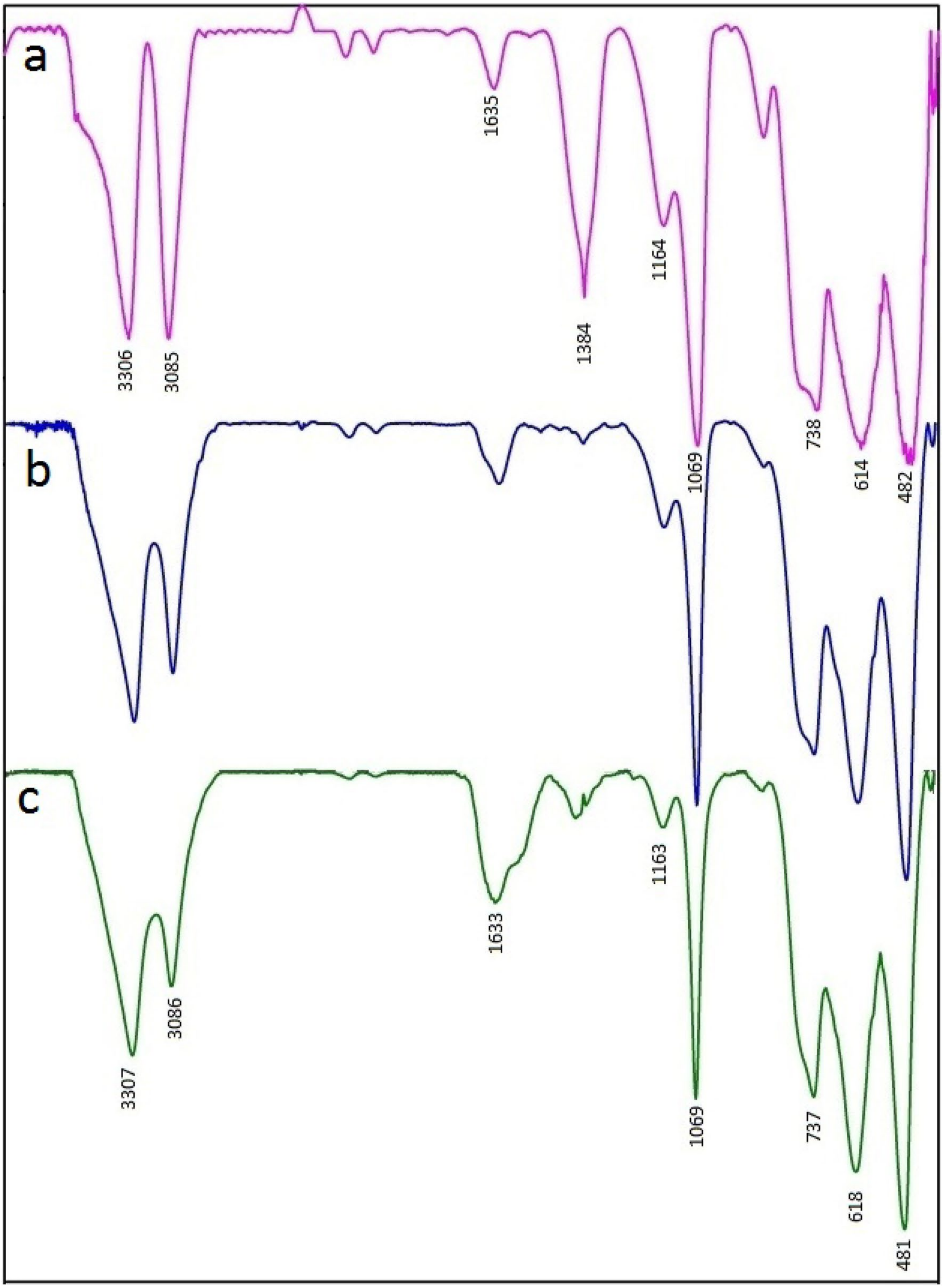


Fig. 6 FT-IR spectra of, **a** boehmite, **b** Arg-boehmite and **c** Pd(0)-Arg-boehmite

Scheme 2 C–C coupling reaction through Suzuki reaction in the presence of Pd(0)-Arg-boehmite

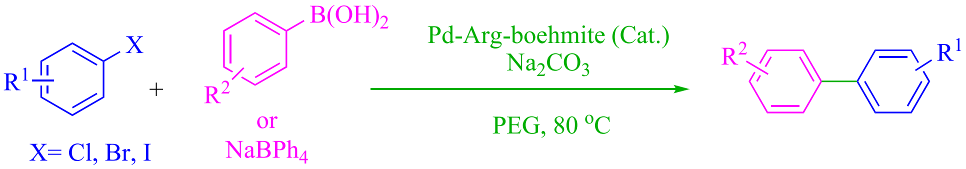


Table 1 Optimization of reaction conditions for the C–C coupling reaction of iodobenzene with $PhB(OH)_2$

Entry	Catalyst (mg)	Solvent	Base	Temperature (°C)	Time (min)	Yield (%)[a]
1	–	PEG	Na_2CO_3	80	600	No reaction
2	6	PEG	Na_2CO_3	80	100	97
3	8	PEG	Na_2CO_3	80	45	98
4	10	PEG	Na_2CO_3	80	40	97
5	8	DMF	Na_2CO_3	80	40	93
6	8	H_2O	Na_2CO_3	80	85	90
7	8	DMSO	Na_2CO_3	80	50	96
8	8	Dioxane	Na_2CO_3	80	180	31
9	8	PEG	NaOEt	80	50	Trace
10	8	PEG	KOH	80	50	42
11	8	PEG	Et_3N	80	50	69
12	8	PEG	Na_2CO_3	60	100	64
13	8	PEG	Na_2CO_3	40	100	Trace
14	8	PEG	Na_2CO_3	r.t	180	Trace

[a] Isolated yields

revealed more accurate information about morphology and particles size of the palladium nanoparticles. As shown in Fig. 2, most of the palladium nanoparticles are in nano size with an average diameter about 5–7 nm.

In order to show the types of elements in catalyst, the EDS analysis of Pd(0)-Arg-boehmite has been examined (Fig. 3). As shown in Fig. 3, Al, O, C, N and Pd species were observed in the catalyst structure.

In order to quantitative analysis and find out the exact amount of palladium, ICP-OES has been performed. According to the ICP analysis, the exact amount of palladium supported on Arg-boehmite is estimated (1.35×10^{-3} mol/g).

The XRD patterns of boehmite nanoparticles and Pd(0)-Arg-boehmite are shown in Fig. 4. Which the boehmite phase was characterized by the 2θ values at 14.40, 28.41, 38.55, 46.45, 49.55, 51.94, 56.02, 59.35, 65.04, 65.56, 68.09, and 72.38 from the XRD patterns, which these peaks are related to (0 2 0), (1 2 0), (0 3 1), (1 3 1), (0 5 1), (2 0 0), (1 5 1), (0 8 0), (2 3 1), (0 0 2), (1 7 1), and (2 5 1) reflections, respectively which is in a good agreement with standard boehmite XRD spectrum and the all peaks can be confirmed the crystallization of boehmite with an orthorhombic unit cell [31]. Also, it could be seen that the boehmite phase has not been destroyed during the modifications.

Qualitative determination of the organic groups grafted on the boehmite surface was studied by TGA analysis with a heating rate of 10 °C/min in the range 30–800 °C. TGA curves of boehmite nanoparticles and Pd(0)-Arg-boehmite are shown in Fig. 5. The TGA curve of boehmite nanoparticles showed a 6% weight loss from 25 to 250 °C, which is related to desorption of water and hydroxyl groups. The TGA curve of the Pd(0)-Arg-boehmite shows the mass loss of the organic functional group as it decompose upon heating (Fig. 5). The TGA analysis of catalyst showed three decreasing peaks. The first one that appeared at low temperature shows a weight loss of 5% which is probably related to the physically adsorbed solvents on the surface of particles [25, 32]. Second peak has appeared at 250–450 °C which corresponded to the loss of the organic spacer group and palladium complex grafted on boehmite nanoparticles. Final weight loss about 11% between 500 and 800 °C may be related to the transformation of thermal crystal phase of boehmite particles.

Figure 6 shows the FT-IR spectrums of boehmite, Arg-boehmite and Pd(0)-Arg-boehmite. The FT-IR spectrum of the boehmite nanoparticles (Spectrum a) shows two strong bands at 3085 and 3306/cm, which are attributed to the both symmetrical and asymmetrical modes of the O–H bonds on the surface of boehmite nanoparticles [25]. In FT-IR spectrums a–c, several peaks that appear at 481, 615

Table 2 Results of Suzuki reaction in the presence of catalytic amounts of Pd(0)-Arg-boehmite under optimized condition

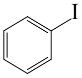
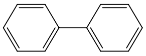
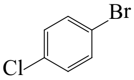
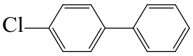
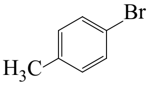
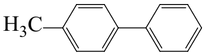
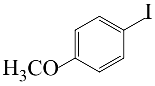
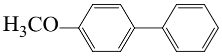
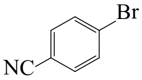
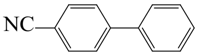
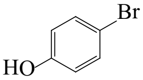
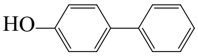
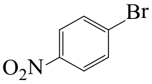
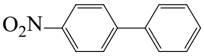
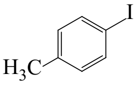
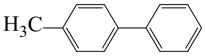
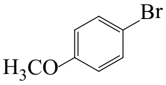
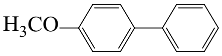
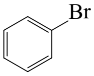
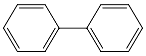
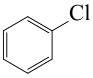
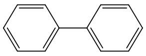
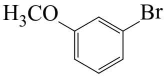
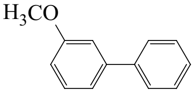
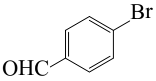
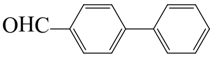
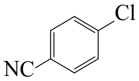
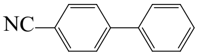
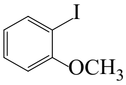
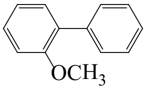
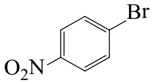
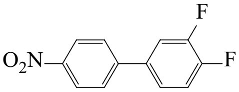
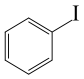
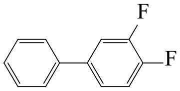
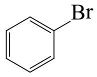
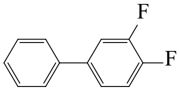
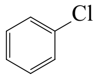
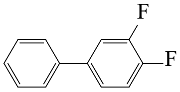
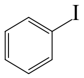
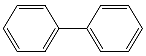
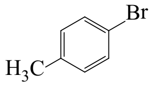
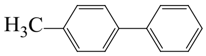
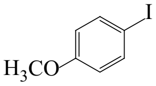
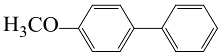
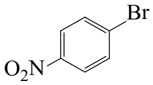
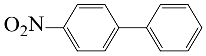
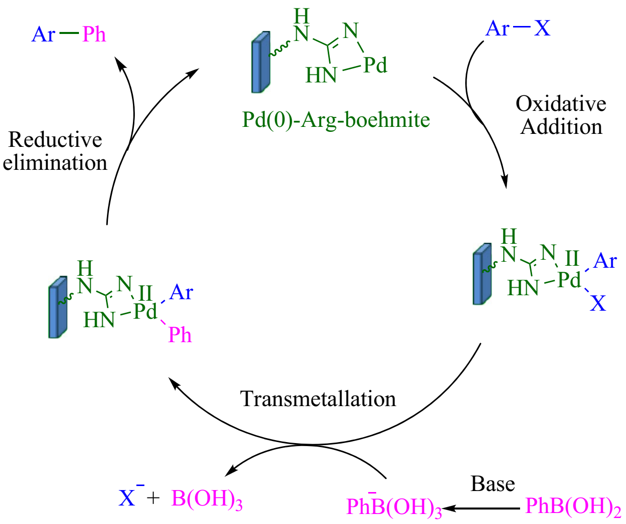
Entry	Aryl halide	Phenylating reagent	Product	Time (min)	Yield (%)^a	TOF (h^{-1})
1		$C_6H_5B(OH)_2$		45	98	121
2		$C_6H_5B(OH)_2$		40	97	134.7
3		$C_6H_5B(OH)_2$		50	95	105.5
4		$C_6H_5B(OH)_2$		70	97	77
5		$C_6H_5B(OH)_2$		170	94	30.7
6		$C_6H_5B(OH)_2$		80	92	63.9
7		$C_6H_5B(OH)_2$		110	96	48.5
8		$C_6H_5B(OH)_2$		240	91	21.1
9		$C_6H_5B(OH)_2$		400	93	12.9
10		$C_6H_5B(OH)_2$		80	94	62.3
11		$C_6H_5B(OH)_2$		140	90	35.7
12		$C_6H_5B(OH)_2$		60	95	88
13		$C_6H_5B(OH)_2$		150	90	33.3
14		$C_6H_5B(OH)_2$		360	81	12.5
15		$C_6H_5B(OH)_2$		50	96	106.7

Table 2 (continued)

Entry	Aryl halide	Phenylating reagent	Product	Time (min)	Yield (%)[a]	TOF (h^{-1})
16		3,4-diF-$C_6H_3B(OH)_2$		70	95	75.4
17		3,4-diF-$C_6H_3B(OH)_2$		60	93	86.1
18		3,4-diF-$C_6H_3B(OH)_2$		70	96	76.2
19		3,4-diF-$C_6H_3B(OH)_2$		110	91	46
20		$NaBPh_4$		30	96[b]	177.8
21		$NaBPh_4$		50	95[b]	105.6
22		$NaBPh_4$		60	97[b]	89.8
23		$NaBPh_4$		95	93[b]	54.4

[a] Isolated yield

[b] Reaction conditions: aryl halide (1 mmol), Pd(0)-Arg-boehmite (8 mg,1.08 mol%), sodium tetraphenyl borate (0.5 mmol) and Na_2CO_3 (3 mmol) in PEG at 80 °C



Scheme 3 Mechanism of the Pd(0)-Arg-boehmite catalyzed Suzuki reaction

and 737/cm can be related to the absorption of Al–O bonds [27]. Also, the nitrate impurity vibration at 1633/cm and the vibrations of hydrogen bands OH⋯OH by two strong absorption bands at 1164 and 1069/cm were observed in FT-IR spectrum [31]. The FT-IR spectra of catalyst was indicated that the boehmite phase has not been destroyed during the modifications.

3.3 Catalytic Activity of Pd(0)-Arg-boehmite in the C–C Coupling Reactions

As a part of our ongoing program directed towards the catalytic activity of modified boehmite nanoparticles in organic reactions [25, 31], we were interested in finding a simple and efficient method for the carbon–carbon cross coupling reaction in the presence of immobilized Pd-Arginine on boehmite nanoparticles (Pd(0)-Arg-boehmite) as a new and recoverable nanocatalyst. The Suzuki reaction in the presence of this catalyst is shown in Scheme 2.

Scheme 4 Pd(0)-Arg-boehmite catalyzed the Heck reaction

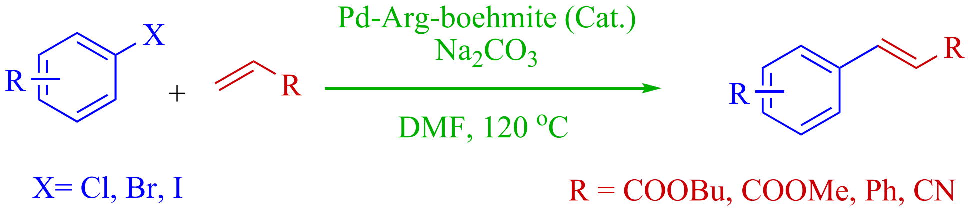


Table 3 Optimization of reaction conditions for the coupling of iodobenzene with butyl acrylate

Entry	Catalyst (mg)	Solvent	Base	Amounts of base (mmol)	Temperature (ºC)	Time (min)	Yield (%)[a]
1	–	DMF	Na_2CO_3	3	120	600	No reaction
2	8	DMF	Na_2CO_3	3	120	150	46
3	14	DMF	Na_2CO_3	3	120	150	64
4	16	DMF	Na_2CO_3	3	120	50	98
5	16	PEG	Na_2CO_3	3	120	100	69
6	16	H_2O	Na_2CO_3	3	100	100	46
7	16	DMSO	Na_2CO_3	3	120	60	96
8	16	EtOH	Na_2CO_3	3	Reflux	100	Trace
9	16	DMF	NaOEt	3	120	60	Trace
10	16	DMF	KOH	3	120	60	31
11	16	DMF	Et_3N	3	120	60	51
12	16	DMF	Na_2CO_3	1.5	120	60	59
13	16	DMF	Na_2CO_3	3	100	60	60
14	16	DMF	Na_2CO_3	3	80	60	36

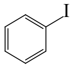
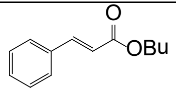
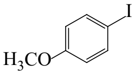
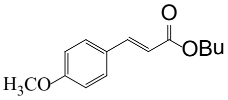
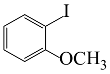
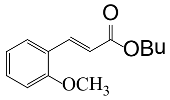
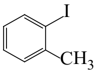
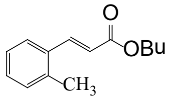
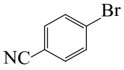
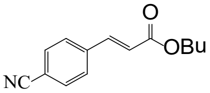
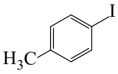
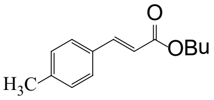
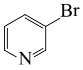
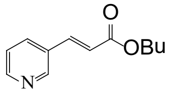
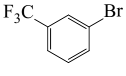
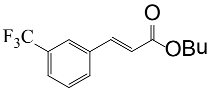
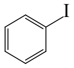
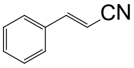
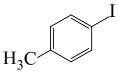
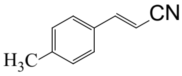
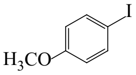
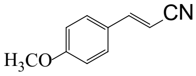
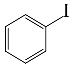
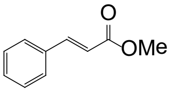
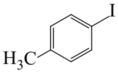
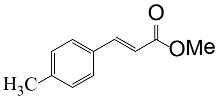
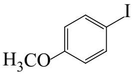
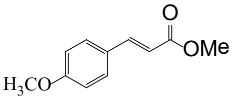
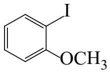
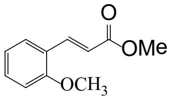
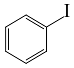
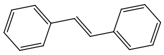
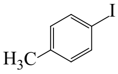
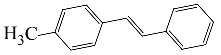
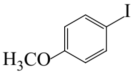
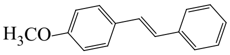
[a] Isolated yields

In order to illustrate the catalytic activity of Pd(0)-Arg-boehmite in the C–C coupling reaction, we first examined the coupling of iodobenzene with phenylboronic acid ($PhB(OH)_2$), and the results are summarized in Table 1. In order to optimize reaction conditions, we examined influvence of different parameters such as solvent, temperature, base, and different amounts of Pd(0)-Arg-boehmite, on the outcome of C–C coupling reaction of iodobenzene and phenylboronic acid. The results show that the reaction cannot proceed in the absence of Pd(0)-Arg-boehmite even running the reaction for 10 h, (Table 1, entry 1). In order to choose the reaction media, different solvents such as PEG, DMF, DMSO, H_2O and dioxane were screened (Table 1, entries 4–8) and the best results were obtained in PEG using 0.008 g (1.08 mol%) of Pd(0)-Arg-boehmite (Table 1, entry 3). Also, the effect of base were studied which in the presence of Na_2CO_3 at 80 °C quantitative conversion of product was observed (Table 1, entry 3). But, when the other bases (such as NaOEt, KOH, and Et_3N) were employed, suitable yield was not detected in comparison to Na_2CO_3 (Table 1, entries 9–11). Also, we found that the coupling reaction yields were susceptible to temperature changes. Therefore, the effect of temperature were studied (Table 1, entries 12–14). The results shown that at room temperature the reaction cannot proceed even running the reaction for 3 h (Table 1, entry 14), and the best results were obtained at 80 °C (98% of yield), while conversion reduced to 64% at 60 °C (Table 1, entry 12).

Aiming to extend the scope of our methodology, we next used different aryl halides as coupling partner for this cross coupling reaction. The results are summarized in Table 2. Thus, various aryl iodides and bromides were coupled with phenylboronic acid and converted into corresponding biphenyls. We also examined the cross coupling reaction of several substituted aryl chlorides with phenylboronic acid under the optimized reaction conditions. However, aryl bromides and aryl iodides show lower reaction times in comparison with those corresponding aryl chlorides. In order to show the chemoselectivity of the presented protocol, 1-chloro-4-bromobenzene was coupled with phenylboronic acid. Interestingly, chloro- group remained intact during the coupling reaction, while the bromo- group was coupled successfully. The results revealed that this methodology is effective for a wide range of aryl halide including Cl, Br and I; however, aryl chlorides showed less reactivity toward the coupling reaction than their aryl iodides and bromides analogs.

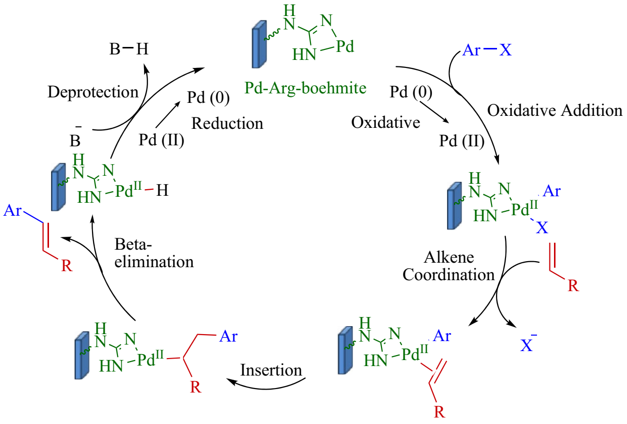
After this pioneering examples, we also applied optimized reaction conditions for the coupling of aryl halides with 3,4-difluoro phenylboronic acid (Table 2, entries

Table 4 Coupling of aryl halides with butyl acrylate, methyl acrylate, styrene or acrylonitrile in the presence of catalytic amounts of Pd(0)-Arg-boehmite

Entry	Aryl halide	Product	Time (min)	Yield (%)[a]	TOF (h^{-1})
1			50	98	54.4
2			250	94	10.4
3			300	95	8.8
4			230	88	10.6
5			350	94	7.5
6			60	97	44.9
7			60	89	41.2
8			420	91	6
9			80	97	33.7
10			200	94	13.1
11			140	96	19
12			140	96	19
13			150	97	18
14			120	98	22.7
15			240	98	11.3
16			18h[b]	77	1.9
17			18h[b]	72	1.4
18			18h[b]	73	1.5

[a] Isolated yield

[b] Reaction conditions: aryl halide (1 mmol), Pd(0)-Arg-boehmite (20 mg, 2.7 mol%), alkene (1.2 mmol) and K_2CO_3 (3 mmol) in DMF at 120 °C



Scheme 5 Pd(0)-Arg-boehmite catalyzed the Heck reaction

16–19) and sodium tetraphenyl borate ($NaBPh_4$) (Table 2, entries 20–23) and the corresponding biphenyls were obtained in short reaction times with good to excellent yields.

Catalytic cycle for Suzuki reaction in the presence of Pd(0)-Arg-boehmite was outlined in Scheme 3.

In order to extend the catalytic activity of Pd(0)-Arg-boehmite, we report the application of Pd(0)-Arg-boehmite as catalyst for the Heck reaction via coupling of various aryl halides with butyl acrylate, methyl acrylate, acrylonitrile and styrene (Scheme 4). In order to optimize the reaction conditions, the coupling of iodobenzene with butyl acrylate was studied in the presence of different amounts of catalyst (Table 3, entries 1–4) and in the various solvents such as H_2O, DMSO, PEG and DMF (Table 3, entries 4–8). The best result was obtained in the presence of 16 mg (2.16 mol%) of Pd(0)-Arg-boehmite in DMF. The reaction was also carried out with the little amount of catalyst (Table 3, entries 2, 3), but in these cases only low yields of the C–C coupled products were obtained. The reaction was significantly affected by the nature of base and the additive. Therefore, the effect and amount of base on the outcome of the reaction was explored (Table 3, entries 9–12). We found that Na_2CO_3 afforded the best results for this reaction and allowed the coupling product obtained in 98% yield after 50 min (Table 3, entry 4). The other bases such as NaOEt, KOH, and Et_3N were not as effective as Na_2CO_3, only afforded moderate to low yields of corresponding coupling product. Also when the amount of Na_2CO_3 was reduced to 1.5 mmol, the yield of the reaction decreased to 59%. Finally, the effect of temperature was examined, which undesirable results were observed at 80 and 100 °C (Table 3, entries 13, 14). Therefore, the best results were obtained in DMF at 120 °C for 50 min in the presence of 16 mg (2.16 mol%) of Pd(0)-Arg-boehmite using 3 mmol of Na_2CO_3 (Table 3, entry 4).

This optimized conditions were also applied for the coupling of other aryl halides including electron-donor and electron-withdrawing functional groups with butyl acrylate to afford the corresponding products and the all products were obtained in good yields (Table 4, entries 1–8).

We also applied optimized reaction conditions for the coupling of aryl halides with acrylonitrile (Table 4, entries 9–11), methyl acrylate (Table 4, entries 12–15) and styrene (Table 4, entries 16–18). The electron-neutral, electron-rich

Table 5 Recyclability of Pd(0)-Arg-boehmite in the coupling of iodobenzene with $PhB(OH)_2$

Run no.	1	2	3	4	5	6
Time (min)	45	45	50	60	70	95
Yield	98	98	95	97	94	93

Table 6 Comparison results of Pd(0)-Arg-boehmite with other catalysts for the coupling of iodobenzene with phenylboronic acid

Entry	Catalyst	Condition	Time (h)	Yield (%)	TOF (/h)	Refs.
1	LDH-Pd(0)	K_2CO_3, 1,4-dioxane: H_2O (5:1), 80 °C	10	96	–	[33]
2	Pd NP	H_2O, KOH, 100 °C	12	95	7.9	[34]
3	Pd(II)-NHC complex	DMF, Cs_2CO_3, 100 °C	24	99	4.1	[35]
4	CA/Pd(0)	H_2O, K_2CO_3, 100 °C	2	94	94	[36]
5	*N,N'*-bis(2-pyridinecarboxamide)-1,2-benzene palladium complex	H_2O, K_2CO_3, 100 °C	3	97	32	[37]
6	NHC-Pd(II) complex	THF, Cs_2CO_3, 80 °C	12	88	7.3	[38]
7	Pd/Au NPs	EtOH/H_2O, K_2CO_3, 80 °C	24	88	3.6	[39]
8	Pd-MPTAT-1	NaOH, DMF: H_2O (1:5), 85 °C	8	95	–	[40]
9	PANI-Pd	K_2CO_3, 1,4-dioxane: H_2O (1:1), 95 °C	4	91	10.3	[41]
10	Pd(0)-Arg-boehmite	PEG, Na_2CO_3, 80 °C	0.75	98	120.9	This work

and electron-poor aryl halides reacted with acrylonitrile, methyl acrylate and styrene efficiently to produce the corresponding coupled products in good to excellent yields. Whereas, styrene has been coupled with aryl halides in the presence of 20 mg (2.7 mol%) of Pd(0)-Arg-boehmite. Therefore, these results revealed that this methodology is effective for a wide range of alkenes and aryl halides.

Catalytic cycle for Heck reaction in the presence of Pd(0)-Arg-boehmite was outlined in Scheme 5.

3.4 Reusability of the Catalyst

The reusability of the catalysts is an important factor for industrial applications. Therefore, the recovery and reusability of Pd(0)-Arg-boehmite was investigated using the reaction of iodobenzene with phenylboronic acid in the presence of described catalyst (Table 5). After completion of the reaction, the catalyst was recovered via centrifugation, washed with ethyl acetate to remove residual product and the catalyst reused for next reactions for at least 6 times without any significant loss of its catalytic activity or palladium leaching. Which clearly demonstrates the practical recyclability of this catalyst.

3.5 Catalyst Leaching Study

The amounts of palladium leaching in reaction mixture was studied by checking the Pd loading amount before and after recycling of the catalyst by ICP-OEIS technique. Based on ICP-OEIS analysis, the amount of palladium in fresh catalyst and the recycled catalyst after 6 times recycling is 1.35 and 1.28 mmol/g, respectively, which indicated that palladium leaching of this catalyst is very low.

In order to perform hot filtration experiment, two reaction of iodobenzene with $PhB(OH)_2$ has been performed under optimized reaction conditions. In the first reaction, the biphenyl was obtained after 22 min (in the half time of the reaction) in 64% yield. Simultaneously in second reaction, the same reaction was repeated, but in the half time of the reaction (after 22 min), the catalyst was removed from the reaction mixture by filtration and the reaction mixture was allowed to run for another 22 min. The yield of reaction in this stage was 66%. These experiments confirmed that Pd(0)-Arg-boehmite are essential for completion of reaction and the leaching of palladium hasn’t been occurred.

3.6 Comparison of the Catalyst

In order to examine the efficiency of these procedures, we compared the results of the coupling of iodobenzene with phenylboronic acid with the previously reported methods in the literature and results are sumarized in Table 6. This catalyst showed shorter reaction time and better yield than other catalysts. Also Pd(0)-Arg-boehmite is comparable in terms of price, non-toxicity, stability and easy separation with other reported catalyst. In addition, the recovery and recycleability of this catalyst is more rapid and easier than the other catalysts. Also, a comparison of activity based on turnover frequency (TOF) showed excellent results for Pd(0)-Arg-boehmite in C–C coupling reactions. As shown in Table 5, Pd(0)-Arg-boehmite was showed a high TOF number in comparison with other catalysts, this results was indicate that Pd(0)-Arg-boehmite is more effective and more efficient in compared to other catalysts. More importantly, in comparison with other catalysts, Pd(0)-Arg-boehmite has been easily prepared using cheap and commercially available materials in a short period of time.

4 Conclusions

In conclusion a novel and efficient heterogeneous catalyst (Pd(0)-Arg-boehmite) was synthesized by direct supportting of Pd-arginine complex on boehmite nanoparticles for the first time. This catalyst was characterized by XRD, TGA, TEM, SEM, EDS and ICP-OES techniques. The Pd(0)-Arg-boehmite exhibits an excellent catalytic activity, high reusability and air- moisture stability for the Suzuki and Heck reactions. This methodology is effective for a wide range of aryl halide including Cl, Br and I. Also the catalyst can be recovered and recycled over 6 times without any significant loss of its activity or palladium leaching.

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