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FULL PAPER

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Biochar as heterogeneous support for immobilization of Pd as efficient and reusable biocatalyst in C–C coupling reactions

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Biochar is a stable and carbon-rich solid which has a high density of carbonyl, hydroxyl and carboxylic acid functional groups on its surface. In this work, the surface of biochar nanoparticles (BNPs) was modified with 3-choloropropyltrimtoxysilane and further 2-(thiophen-2-yl)-1*H*-benzo[*d*]imidazole was anchored on its surface. Then, palladium nanoparticles were fabricated on the surface of the modified BNPs and further the catalytic application was studied as recyclable biocatalyst in carbon–carbon coupling reactions such as Suzuki–Miyaura and Heck–Mizoroki cross-coupling reactions. The structure of the catalyst was characterized using scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy, thermogravimetric analysis, X-ray diffraction and atomic absorption spectroscopy. The catalyst can be reused several times without a decrease in its catalytic efficiency. In addition to the several advantages reported, application of biochar as catalyst support for the first time is a major novelty of the present work.

KEYWORDS

biochar nanoparticles, C–C coupling reactions, Heck reaction, palladium, Suzuki reaction

1 | INTRODUCTION

Recently, nanotechnology has emerged in science, medicine, industry, pharmacy and chemistry.[1–4] In this regard, various nanoparticles have also been applied as catalyst supports due to their special properties such as high surface area and insolubility.[5–7] When the size of particles is decreased, their surface area is increased, which will be lead to high capacity of catalyst loading.[8] Therefore, nanoparticles are widely employed as solid supports for heterogenization of homogeneous catalysts.[1–8] For example, iron oxide,[9] mesoporous silica materials,[10] carbon nanotubes,[11] ionic liquids,[12] polymers,[13] graphene oxide,[14,15] heteropolyacids,[16] boehmite nanoparticles,[17] etc., have been used as catalyst supports; however, all of these materials require chemical procedures and chemical starting materials for their preparation which are expensive and not environmentally friendly. Biochar is a novel type of nanoparticles, which is a stable carbon solid and used in various fields in past few years for science and engineering.[18–20] In fact, biochar (which is called black carbon) is charcoal which is used for soil amendment, reduction in greenhouse gas emissions from soil, adsorption, water retention, agricultural waste recycling, climate change mitigation and energy production.[21–24] Biochar is made via pyrolysis of biological sources such as woody materials, agricultural wastes, green waste, animal manures and other waste products.[21,22] Therefore, it is inexpensive and environmentally friendly. A number of studies have highlighted the benefits of biochar as soil amendment.[25] Surfaces of biochar nanoparticles are covered with carbonyl, hydroxyl and carboxylic acid functional groups.[25,26] The presence of a high density of carbonyl, hydroxyl and carboxylic acid groups on the biochar surface allows the modification of its surface via reaction with dopamine, alkoxysilane and other reagents which can be used as a support for the immobilization of catalysts or other substances. Despite various studies of the morphology, application, properties and preparation of biochar,[18–27] currently no reports are available of the application of biochar as a catalyst support. Biochar is a stable solid in air atmosphere, at high temperature and in aqueous solution, and therefore biochar is an ideal catalyst support for organic processes occurring under harsh conditions. Also, biochar has several advantages such as non-toxicity, ready availability, environmentally friendly, high stability and high surface area.[21–26]

In this regard, we report a new complex of palladium, immobilized on biochar nanoparticles, as an efficient and reusable biocatalyst for C–C cross-coupling reactions. The C–C coupling reaction is one of the most powerful tools for the preparation of natural products, advanced materials, pharmaceuticals, biologically active compounds, polymers, hydrocarbons and liquid crystal materials.[27–32] Suzuki–Miyaura and Heck–Mizoroki reactions are usually reported with homogeneous or heterogeneous palladium catalysts.[33–40] The use of palladium–phosphine catalysts involves expensive, toxic and air- and moisture-sensitive procedures. Therefore, to embrace green chemistry principles, we report a procedure for the immobilization of palladium on biochar nanoparticles as a phosphine-free, stable and recyclable biocatalyst for the Suzuki–Miyaura and Heck–Mizoroki reactions.

2 | EXPERIMENTAL

2.1 | Preparation of biochar

An amount of 500 g of dried chicken manure was placed in a porcelain crucible. The pyrolysis temperature was selected from 400 to 800°C, which is the common temperature range of fast pyrolysis. The set temperature was reached after about 30 min of heating with the carrier gas (N_2) sweeping at 0.3 l min^{-1}, and the porcelain crucible was fed into the heating zone with an N_2 flow rate of 0.03 l min^{-1}. After 1 and 2 h, the pyrolysis process was ended, and the porcelain crucible was removed from the heating zone and cooled with N_2 sweeping at 0.3 l min^{-1} for 30 min. The solid product was biochar, which was ground through a 40 mesh sieve (0.45 mm). Prior to additional experiments, no pre-treatment was performed. The obtained biochar samples were abbreviated as CMB400–1, CMB400–2, CMB600–1, CMB600–2, CMB800–1 and CMB800–2 according to the pyrolysis residence time (1 and 2 h) and temperature.

2.2 | Preparation of catalyst

Initially, 2-(thiophen-2-yl)-1*H*-benzo[*d*]imidazole (TBA) as ligand for immobilization of palladium was synthesized according to the procedure reported by Nagawade and Shinde[41] (Scheme 1).

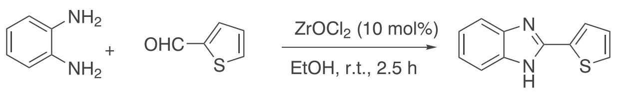
Biochar nanoparticles modified with 3-cholopropyltrimtoxysilane (CPTMS@biochar) were obtained according to a new reported procedure;[42] subsequently CPTMS@biochar (1.0 g) was dispersed in toluene and 1.5 mmol of TBA was added to this mixture. The mixture was stirred at 90°C for 48 h. The solid product (TBA@biochar) was isolated after washing with ethanol and drying at 50°C. TBA@biochar (1.0 g) was dispersed in ethanol and mixed with 0.5 g of $Pd(OAc)_2$. The mixture was stirred at 80°C for 20 h. Finally, $NaBH_4$ (0.5 mmol) was added to the reaction mixture and was allowed to run for another 2 h. The solid product (Pd(0)-TBA@biochar) was obtained after washing with water and ethanol and drying at 50°C.

2.3 | General procedure Suzuki reaction catalysed by Pd(0)-TBA@biochar

Amounts of 1 mmol of aryl halide, 1 mmol of phenylboronic acid or 1 mmol of 3,4-difluorophenylboronic acid, 3 mmol of sodium carbonate and 5 mg of Pd(0)-TBA@biochar (containing 0.715 mol% of Pd) were stirred in PEG-400 at 80°C and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and the catalyst was separated by simple filtration and washed with ethyl acetate. The reaction mixture was extracted with water and ethyl acetate. The organic layer was dried over 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 Heck reaction catalysed by Pd(0)-TBA@biochar

A mixture of aryl halide (1 mmol), butyl acrylate or methyl acrylate or acrylonitrile (1.2 mmol), Na_2CO_3 (3 mmol) and Pd(0)-TBA@biochar (10 mg, containing 1.43 mol% of Pd) was stirred in PEG-400 at 120°C and the progress of the reaction was monitored by TLC. After



SCHEME 1 Synthesis of 2-(thiophen-2-yl)-1*H*-benzo[*d*]imidazole (TBA)

completion of the reaction, the mixture was cooled to room temperature and the catalyst was separated by simple filtration and washed with diethyl ether. The reaction mixture was extracted with water 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 moderate to good yields.

2.5 | Selected spectral data

2.5.1 | 1,4-Diphenylbenzene

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.72–7.70 (d, J = 8 Hz, 4H), 7.68–7.66 (d, J = 8 Hz, 4H), 7.52–7.46 (q, J = 8 Hz, 4H), 7.42–7.36 (q, J = 8 Hz, 2H) ppm.

2.5.2 | 2-Phenylnaphthalene

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.08 (s, 1H), 7.97–7.89 (m, 3H), 7.80–7.75 (m, 3H), 7.57–7.50 (m, 4H), 7.44–7.40 (tt, J = 7.2 Hz, 1.6 Hz, 1H) ppm.

2.5.3 | [1,1′-Biphenyl]-4-carbaldehyde

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 10.09 (s, 1H), 7.99–7.97 (d, J = 8 Hz, 2H), 7.79–7.77 (d, J = 8 Hz, 2H), 7.68–7.66 (d, J = 8 Hz, 2H), 7.53–7.49 (t, J = 8 Hz, 2H), 7.47–7.43 (t, J = 8 Hz, 1H) ppm.

2.5.4 | [1,1′-Biphenyl]-3-carbaldehyde

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 10.12 (s, 1H), 8.40 (s, 1H), 8.15–8.14 (d, J = 2 Hz, 1H), 7.91–7.87 (td, J = 4 Hz, J = 2 Hz, 1H), 7.68–7.65 (m, 2H), 7.62–7.57 (dd, J = 12 Hz, J = 4 Hz, 1H), 7.53–7.49 (t, J = 8 Hz, 2H), 7.45–7.43 (m, 1H) ppm.

2.5.5 | 3,4-Difluoro-1,1′-biphenyl

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.56–7.54 (d, J = 8 Hz, 2H), 7.49–7.45 (t, J = 8 Hz, 2H), 7.44–7.38 (m, 2H), 7.34–7.31 (m,1H), 7.28–7.21 (m, 1H) ppm.

2.5.6 | Butyl 3-(4-methylphenyl)acrylate

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.70–7.66 (d, J = 16 Hz, 1H), 7.46–7.44 (d, J = 8 Hz, 2H), 7.22–7.20 (d, J = 8 Hz, 2H), 6.44–6.40 (d, J = 16 Hz, 1H), 4.25–4.21 (t, J = 8 Hz, 2H), 2.39 (s, 3H), 1.75–1.68 (quint, J = 8 Hz, 2H), 1.51–1.42 (sextet, J = 8 Hz, 2H), 1.01–0.97 (t, J = 8 Hz, 3H) ppm.

2.5.7 | Butyl 3-(4-methoxyphenyl)acrylate

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.67–7.63 (d, J = 16 Hz, 1H), 7.5–7.48 (d, J = 8 Hz, 2H), 6.92–6.90 (d, J = 8 Hz, 2H), 6.34–6.30 (d, J = 16 Hz, 1H), 4.23–4.19 (t, J = 8 Hz, 2H), 3.84 (s, 3H), 1.74–1.66 (quint, J = 4 Hz, 2H), 1.50–1.41 (sextet, J = 8 Hz, 2H), 1.00–0.96 (t, J = 8 Hz, 3H) ppm.

2.5.8 | Methyl 3-(4-methoxyphenyl) acrylate

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.69–7.65 (d, J = 16 Hz, 1H), 7.50–7.48 (d, J = 8 Hz, 2H), 6.93–6.91 (d, J = 8 Hz, 2H), 6.35–6.31 (d, J = 16 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H) ppm.

2.5.9 | Methyl 3-(*p*-tolyl)acrylate

^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.71–7.67 (d, J = 16 Hz, 1H), 7.45–7.43 (d, J = 8 Hz, 2H), 7.22–7.20 (d, J = 8 Hz, 2H), 6.44–6.40 (d, J = 16 Hz, 1H), 3.82 (s, 3H), 2.39 (s, 3H) ppm.

2.5.10 | 3-(*p*-Tolyl)acrylonitrile

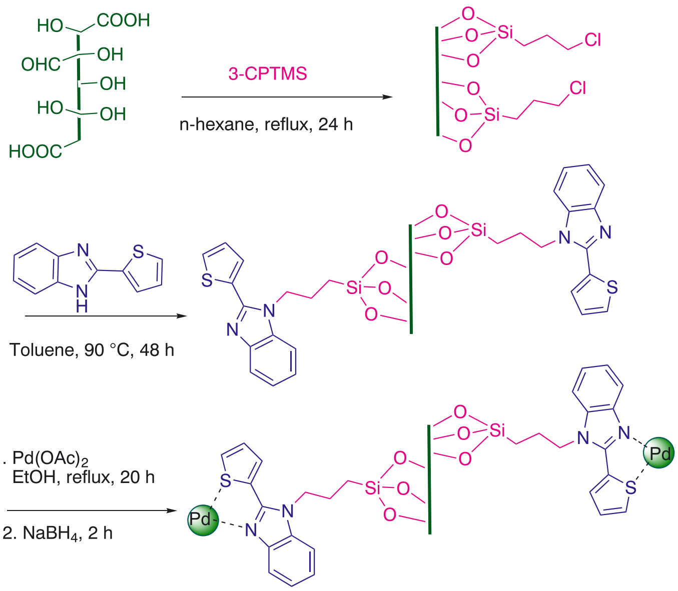
^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.41–7.37 (d, J = 16 Hz, 1H), 7.37–7.34 (m, 2H), 7.25–7.20 (m, 2H), 5.86–5.82 (d, J = 16 Hz, 1H), 2.41 (s, 3H) ppm. Supporting Information.

3 | RESULTS AND DISCUSSION

Pd(0)-TBA@biochar was prepared based on the concise route outlined in Scheme 2. Firstly, biochar was prepared from pyrolysis of chicken manure. Secondly, the surface of the biochar was modified with CPTMS. Subsequently, the terminal chloro groups attached on surface of biochar were functionalized with TBA (TBA@biochar). Finally, the catalyst (Pd(0)-TBA@biochar) was prepared by complexation of TBA@biochar with palladium acetate. This work has several novelties such as: (1) first time applying biochar as a support for a catalyst, (2) first report of using a reusable biocatalyst based on biochar in organic reactions and (3) first time of supporting a metal complex on biochar nanoparticles.

3.1 | Catalyst characterization

After the preparation of the catalyst, it was characterized using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), thermogravimetric analysis (TGA), X-ray diffraction (XRD) and atomic



SCHEME 2 Synthesis of Pd(0)-TBA@biochar

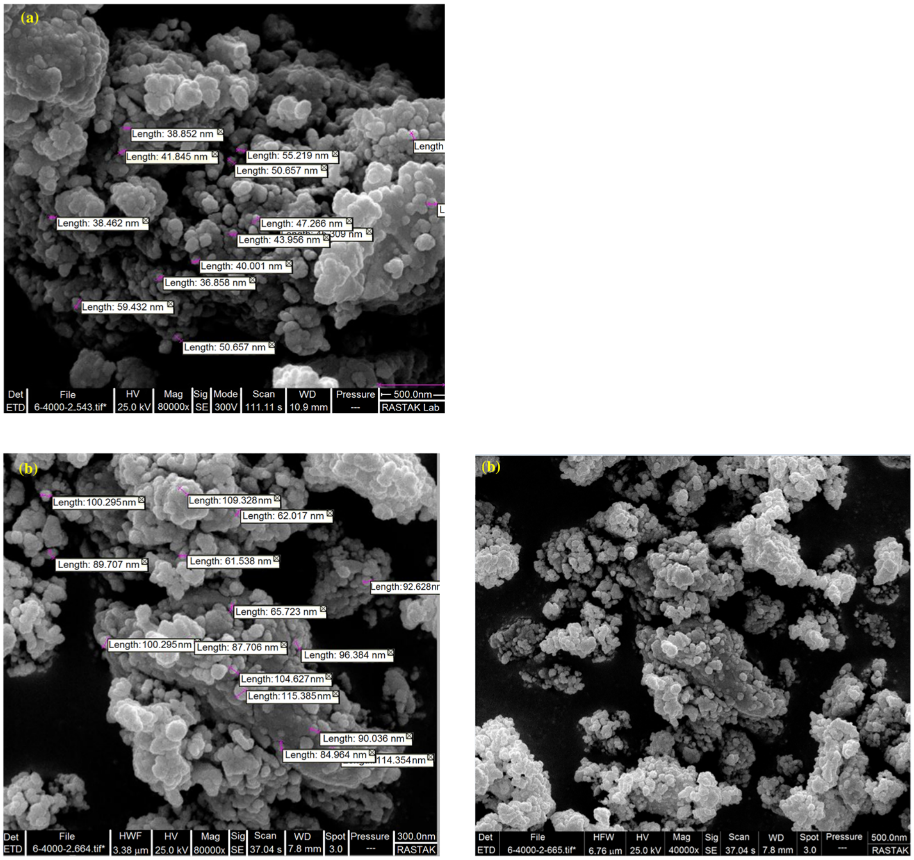


FIGURE 1 SEM images of (a) biochar and (b) Pd(0)-TBA@biochar

absorption spectroscopy (AAS). SEM images of biochar and Pd(0)-TBA@biochar are shown in Figure 1. As shown in Figure 1, biochar and catalyst were prepared with particles of 30–70 nm of diameter with quasi-spherical morphology. The SEM images of biochar (Figure 1a) and of catalyst (Figure 1b) show good agreement in size and shape of particles, which confirms that the biochar is not changed during the modification. Also, TEM images of Pd(0)-TBA@biochar are shown in Figure 2. It can be seen the catalyst was obtained with average size of less than 100 nm. As shown in Figure 2, palladium particles are present in the structure of the catalyst, and the average size of these particles is between 6 and 8 nm.

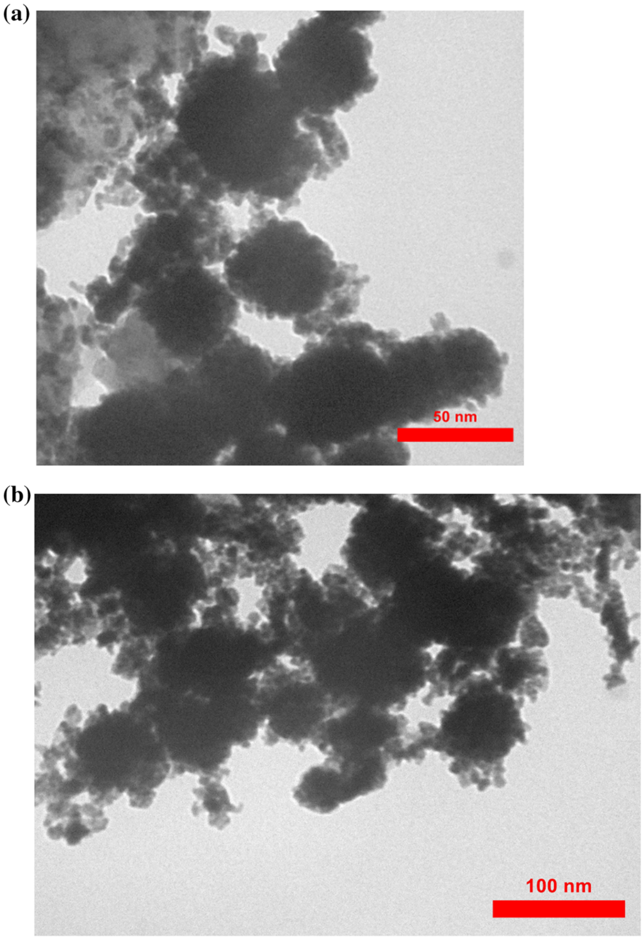


FIGURE 2 TEM images of Pd(0)-TBA@biochar

In order to determine the content of elements in the catalyst, EDS analysis of Pd(0)-TBA@biochar was performed (Figure 33). As depicted, the EDS spectrum of the catalyst shows the presence of C, Si, O, S, N and as well as Pd species in the catalyst. Also, the exact amount of palladium (which is immobilized on the modified biochar nanoparticles) was obtained using the AAS technique and was found to be 1.43×10^{-3} mol g^{-1}.

The TGA diagram of biochar is shown in Figure 4a and that of Pd(0)-TBA@biochar is shown in Figure 4b. The small weight loss of about 5% below 100°C is related to evaporation of solvents and hydroxyl groups on the surface of biochar.[43] The organic contents were decomposed at 200–600°C. As shown in Figure 4b, the weight loss of Pd(0)-TBA@biochar is higher than that of biochar nanoparticles which is associated with the immobilized organic layers on the surface of biochar. This result is strong evidence that organic layers and palladium complex were supported on the surface of biochar nanoparticles.

XRD patterns of biochar and Pd(0)-TBA@biochar are shown in Figure 5 with the diffracted beam as the intensity as a function of the Bragg angle (2θ). The XRD pattern of biochar (Figure 5a) indicates crystallinity with a sharp peak at $2\theta = 30°$.[18] The XRD pattern of biochar also shows several weak peaks at $2\theta = 40.7°$, 43.7°, 48.7° and 66.7°.[18] As shown in Figure 5b, the XRD pattern of Pd(0)-TBA@biochar shows a good agreement with XRD pattern of biochar nanoparticles, from which result it is revealed that the surface modification of the biochar did not destroy its crystallinity. Also the XRD pattern of Pd(0)-TBA@biochar (Figure 5b) shows three peaks (39.5°, 46.1° and 67.5°) which are indexed to Pd(0) on the surface of biochar nanoparticles.[6,33]

3.2 | Catalytic activity of Pd(0)-TBA@biochar in C–C coupling reactions

In order to determine the catalytic activity of Pd(0)-TBA@biochar, we investigated the catalytic C–C coupling reaction of aryl halides with phenylboronic acid ($PhB(OH)_2$) or 3,4-difluorophenylboronic acid ($3,4\text{-diF-}C_6H_3B(OH)_2$) (Scheme 3) and also butyl acrylate, methyl acrylate or acrylonitrile (Scheme 5 in the presence of this catalyst.

To optimize the Suzuki coupling reaction, the reaction of 4-iodotoluene with $PhB(OH)_2$ was selected as a model reaction. This model reaction was investigated in the presence of various amounts of Pd(0)-TBA@biochar

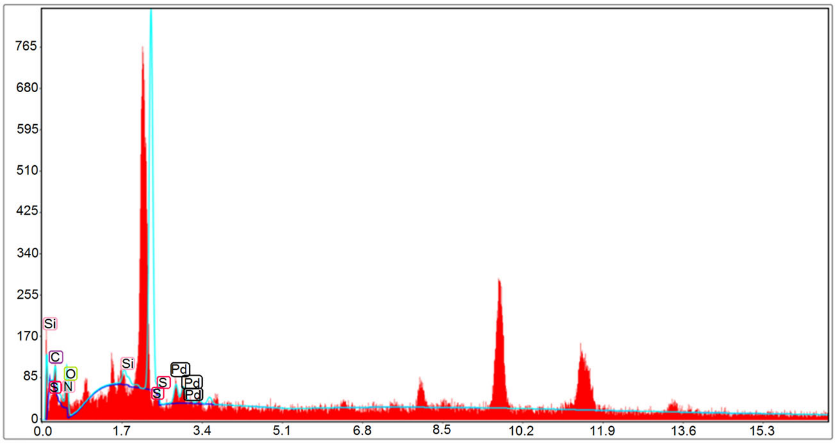


FIGURE 3 EDX spectrum of Pd(0)-TBA@biochar

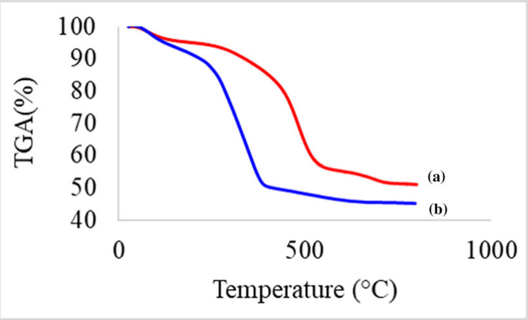


FIGURE 4 TGA diagrams of (a) biochar and (b) Pd(0)-TBA@biochar

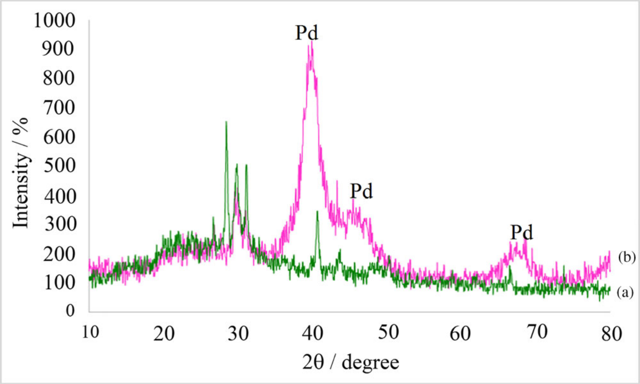


FIGURE 5 XRD patterns of (a) biochar and (b) Pd(0)-TBA@biochar

and the optimal amount of catalyst was found to be 5 mg (0.715 mol% of Pd) of Pd(0)-TBA@biochar (Table 1, entry 3). As evident from Table 1, lower amounts of Pd(0)-TBA@biochar led to a lower yield of product (Table 1, entry 2) and also a higher amount of this catalyst gave no significant improvement in the time or yield of reaction (Table 1, entry 4). In the next step, the model reaction was carried out in various solvents and with various bases (Table 1, entries 5–11). Based on the obtained results, PEG-400 as solvent and sodium carbonate (Na_2CO_3) as base gave the best conversion of starting materials to products. In the final step, the effect of temperature on the model reaction was studied, and the best results were obtained at 80°C (Table 1, entries 11–13).

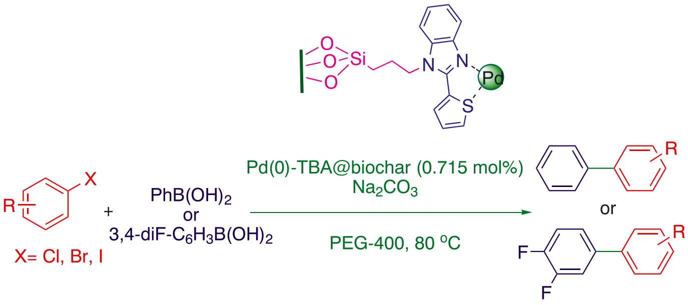
With the optimal reaction conditions in hand, the scope of other *meta*-, *ortho*- and *para*-substituted functional groups on the aromatic ring of aryl halide (involving of Cl, Br and I) was examined (Table 2). Both electron-donating groups such as OH, NH_2, OCH_3 or CH_3 and electron-withdrawing groups such as NO_2, CN, CHO, Cl, COOH or CF_3 reacted conveniently, and the corresponding products were obtained in good to excellent yields and with high turnover frequency (TOF) values. The major advantages are high TOFs and excellent yields of products in short reaction times. In order to extend this work, the coupling of aryl halides with 3,4-diF-$C_6H_3B(OH)_2$ was investigated (Table 2, entries 22–29). In this stage corresponding products were obtained in good to excellent yields. These results revealed that this catalyst can be used for the synthesis of a wide range of biphenyls by coupling of various aryl halides with phenylboronic acid derivatives.

The catalytic cycle for the Suzuki reaction in the presence of Pd(0)-TBA@biochar is shown in Scheme 4. Initially, an oxidative addition of aryl halide to palladium(0) catalyst forms the intermediate **I** which includes palladium(II). Next, transmetallation of **I** gives intermediate **II**. Finally, the reductive elimination of **II** leads to biphenyls as products and regeneration of the catalyst.

Additionally, we studied the catalytic activity of Pd(0)-TBA@biochar in the Heck C–C reaction involving the coupling of aryl halides with various alkenes such as butyl acrylate, methyl acrylate or acrylonitrile (Scheme 5).

In order to optimize the Heck C–C coupling reaction conditions, the coupling of iodobenzene with butyl acrylate was selected as a model reaction. The results summarized in Table 3 indicate that the best outcome was obtained with the use of Na_2CO_3 (3 mmol, 0.318 mg) as base and PEG-400 as solvent in the presence of Pd(0)-TBA@biochar (10 mg, 1.43 mol%) at 120°C (Table 3, entry 3). When the model reaction was examined at 100°C (Table 3, entry 14), the reaction was negatively affected (the yield of product was decreased from 98 to 64%). The yield of obtained product was decreased from 98 to 84% when the amount of Pd(0)-TBA@biochar was decreased to 7 mg (Table 3, entry 2). Also, among the various solvents (water, toluene, 1,4-dioxane, PEG, DMF and DMSO), the best results were obtained in PEG-400 as solvent (Table 3, entries 4–9).

Under the optimized reaction conditions, we next investigated this reaction with other aryl halides bearing



SCHEME 3 Suzuki C–C coupling reaction in the presence of Pd(0)-TBA@biochar

TABLE 1 Optimizing reaction conditions for Suzuki reaction in the presence of Pd(0)-TBA@biochar

Entry	Solvent	Catalyst (mg)	Base	Temperature (°C)	Time (min)	Yield (%)^a
1	PEG	—	Na_2CO_3	80	100	No reaction
2	PEG	3	Na_2CO_3	80	60	88
3	PEG	5	Na_2CO_3	80	20	97
4	PEG	7	Na_2CO_3	80	15	95
5	H_2O	5	Na_2CO_3	80	100	88
6	DMSO	5	Na_2CO_3	80	70	95
7	DMF	5	Na_2CO_3	80	90	91
8	1,4-Dioxane	5	Na_2CO_3	80	120	71
9	PEG	5	KOH	80	60	72
10	PEG	5	NaOEt	80	60	41
11	PEG	5	Et_3N	80	60	69
12	PEG	5	Na_2CO_3	60	60	46
13	PEG	5	Na_2CO_3	40	60	Trace

[a] Isolated yield.

TABLE 2 C–C coupling reaction for synthesis of biphenyl derivatives catalysed by Pd(0)-TBA@biochar

Entry	Aryl halide	Phenylating reagent	Time (min)	Yield (%)^a	TON	TOF (h^{-1})	Melting point (°C)	Reported melting point (°C)
1	Iodobenzene	$C_6H_5B(OH)_2$	125	96	134	64	66–68	66–68[33]
2	Bromobenzene	$C_6H_5B(OH)_2$	140	94	131	56	65–67	66–68[33]
3	Chlorobenzene	$C_6H_5B(OH)_2$	25 h	89	124	5	65–67	66–68[33]
4	4-Iodotoluene	$C_6H_5B(OH)_2$	20	97	135	405	44–46	45–47[39]
5	2-Iodotoluene	$C_6H_5B(OH)_2$	190	91	127	40	Oil	Oil[8]
6	4-Bromochlorobenzene	$C_6H_5B(OH)_2$	85	93	130	92	70–72	71–73[6]
7	4-Bromonitrobenzene	$C_6H_5B(OH)_2$	105	95	133	76	111–113	113–115[9]
8	4-Bromophenol	$C_6H_5B(OH)_2$	115	89	124	65	159–162	162–164[47]
9	4-Bromobenzonitrile	$C_6H_5B(OH)_2$	120	90	126	63	82–83	80–84[42]
10	4-Iodoanisole	$C_6H_5B(OH)_2$	105	95	133	76	80–82	82–84[42]
11	2-Iodoanisole	$C_6H_5B(OH)_2$	170	87	121	43	Oil	Oil[6]
12	4-Bromobenzaldehyde	$C_6H_5B(OH)_2$	180	96	134	45	53–55	55–57[8]
13	4-Bromoaniline	$C_6H_5B(OH)_2$	25 h	90	126	5	52–54	53–54[47]
14	4-Bromoanisole	$C_6H_5B(OH)_2$	24 h	89	124	5	80–83	81–83[48]
15	3-Bromoanisole	$C_6H_5B(OH)_2$	125	92	129	62	Oil	Oil[9]
16	4-Bromotoluene	$C_6H_5B(OH)_2$	45	90	126	168	44–46	43–45[49]
17	1,4-Dibromobenzene	$C_6H_5B(OH)_2$	240	64	89	22	210–212	212–214[50]
18	3-Bromobenzaldehyde	$C_6H_5B(OH)_2$	195	91	127	39	Oil	Oil[9]
19	1-Bromo-3-(trifluoromethyl)benzene	$C_6H_5B(OH)_2$	115	85	119	62	Oil	Oil[6]
20	2-Bromonaphthalene	$C_6H_5B(OH)_2$	380	93	130	20	101–103	104–106[51]

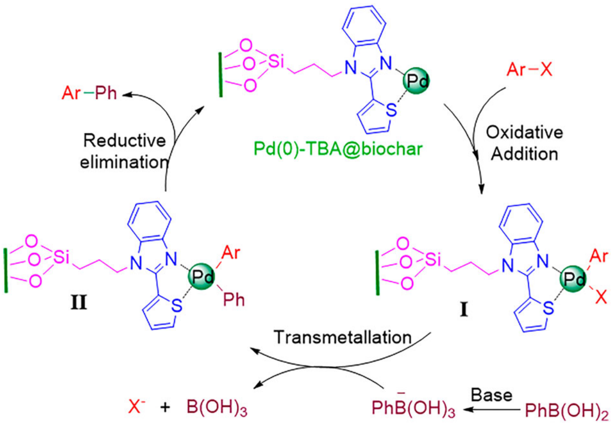
(Continues)

TABLE 2 (Continued)

Entry	Aryl halide	Phenylating reagent	Time (min)	Yield (%)[a]	TON	TOF (h^{-1})	Melting point (°C)	Reported melting point (°C)
21	4-Bromobenzoic acid	$C_6H_5B(OH)_2$	340	91	127	22	219–223	219–224[52]
22	Iodobenzene	3,4-diF-$C_6H_3B(OH)_2$	85	96	134	95	38–41	39–41[33]
23	Bromobenzene	3,4-diF-$C_6H_3B(OH)_2$	235	90	126	32	38–41	39–41[33]
24	4-Iodotoluene	3,4-diF-$C_6H_3B(OH)_2$	90	92	127	86	42–43	—
25	4-Bromonitrobenzene	3,4-diF-$C_6H_3B(OH)_2$	145	95	133	55	118–120	119–120[33]
26	4-Bromobenzonitrile	3,4-diF-$C_6H_3B(OH)_2$	165	91	127	46	105–106	—
27	3-Bromoanisole	3,4-diF-$C_6H_3B(OH)_2$	75	85	119	95	Oil	—
28	4-Bromochlorobenzene	3,4-diF-$C_6H_3B(OH)_2$	70	96	134	115	59	—
29	4-Iodoanisole	3,4-diF-$C_6H_3B(OH)_2$	60	83	116	116	Oil	—

[a] Isolated yield.

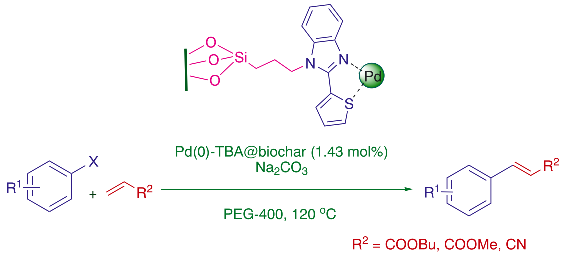
electron-donating and electron-withdrawing groups at the *meta*, *ortho* and *para* positions of aromatic ring of aryl halides (Table 4). In order to extend this work, coupling of aryl halides with methyl acrylate, acrylonitrile and butyl acrylate was investigated, and all products were obtained in good to excellent yields and high TOF values. Therefore this procedure can be applied for coupling of various aryl halides with a variety of alkenes. The catalytic activity of Pd(0)-TBA@biochar showed good selectivity in the coupling of alkenes with aryl iodides in comparison with aryl bromides or aryl chlorides.



SCHEME 4 Suggested mechanism for Suzuki reaction in the presence of Pd(0)-TBA@biochar

The suggested mechanism for the Heck coupling reaction in the presence of Pd(0)-TBA@biochar is outlined in Scheme 6. In the first step, an oxidative addition of aryl halide to palladium(0) gives intermediate **I**. Then, coordination of alkene with intermediate **I** leads to intermediate **II**, which is converted to intermediate **III** with an insertion. Next, β-elimination of intermediate **III** forms intermediate **IV** and products are formed. Finally, the reduction of intermediate **IV** leads to regeneration of the catalyst.

In order to investigate the chemoselectivity of Pd(0)-TBA@biochar, 1-chloro-4-bromobenzene was coupled with phenylboronic acid and 3,4-difluorophenylboronic acid in the presence of Pd(0)-TBA@biochar (Scheme 7). Interestingly, the chloro group was not coupled, while the bromo group was coupled successfully and 4-chloro-1,1′-biphenyl was obtained as pure product in excellent yield (Table 2, entries 6 and 28).



SCHEME 5 Pd(0)-TBA@biochar-catalysed Heck C–C coupling reaction

TABLE 3 Optimizing reaction conditions for Heck reaction in the presence of Pd(0)-TBA@biochar

Entry	Solvent	Catalyst (mg)	Base	Temperature (°C)	Time (min)	Yield (%)[a]
1	PEG	—	Na_2CO_3	120	180	No reaction
2	PEG	7	Na_2CO_3	120	180	84
3	PEG	10	Na_2CO_3	120	70	98
4	PEG	12	Na_2CO_3	120	60	93
5	Toluene	10	Na_2CO_3	Reflux	70	62
6	H_2O	10	Na_2CO_3	Reflux	70	74
7	DMF	10	Na_2CO_3	120	70	82
8	DMSO	10	Na_2CO_3	120	70	79
9	1,4-Dioxane	10	Na_2CO_3	Reflux	70	52
10	PEG	10	NaOEt	120	70	35
11	PEG	10	Et_3N	120	70	73
12	PEG	10	KOH	120	70	68
13	PEG	10	K_2CO_3	120	70	83
14	PEG	10	Na_2CO_3	100	70	64

[a] Isolated yield

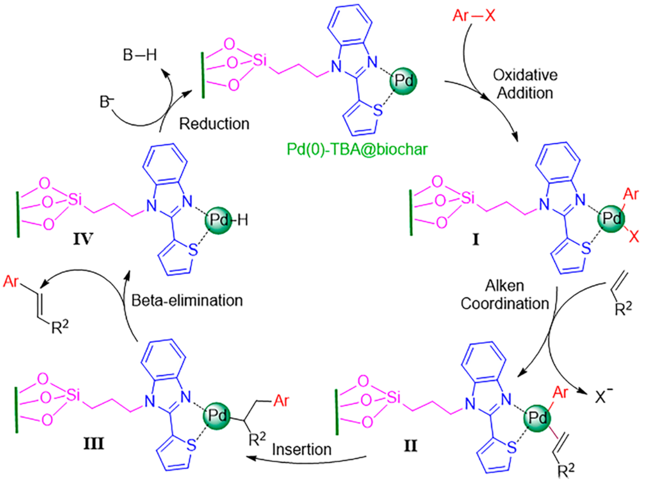
TABLE 4 Coupling of aryl halides with butyl acrylate, methyl acrylate and acrylonitrile catalysed by Pd(0)-TBA@biochar

Entry	Aryl halide	Alkene	Time (min)	Yield (%)[a]	TON	TOF (h^{-1})	Melting point (°C)	Reported melting point (°C)
1	Iodobenzene	Butyl acrylate	70	98	68	59	Oil	Oil[53]
2	4-Iodotoluene	Butyl acrylate	80	96	67	50	Oil	Oil[6]
3	2-Iodotoluene	Butyl acrylate	200	91	64	19	Oil	Oil[54]
4	4-Iodoanisole	Butyl acrylate	130	93	65	30	Oil	Oil[42]
5	2-Iodoanisole	Butyl acrylate	160	90	63	24	Oil	Oil[8]
6	Iodobenzene	Methyl acrylate	55	95	66	72	Oil	Oil [55]
7	4-Iodotoluene	Methyl acrylate	95	88	61	39	54–56	55–57[56]
8	2-Iodotoluene	Methyl acrylate	155	91	64	25	Oil	[57]
9	4-Iodoanisole	Methyl acrylate	80	93	65	49	86–88	88–91[56]
10	2-Iodoanisole	Methyl acrylate	240	89	62	15	Oil	Oil[58]
11	Iodobenzene	Acrylonitrile	65	97	68	63	Oil	Oil[54]
12	4-Iodotoluene	Acrylonitrile	200	95	66	20	Oil	Oil[54]
13	2-Iodotoluene	Acrylonitrile	180	92	64	21	Oil	Oil[6]
14	4-Iodoanisole	Acrylonitrile	175	93	65	22	Oil	Oil[59]
15	2-Iodoanisole	Acrylonitrile	255	90	63	15	Oil	-

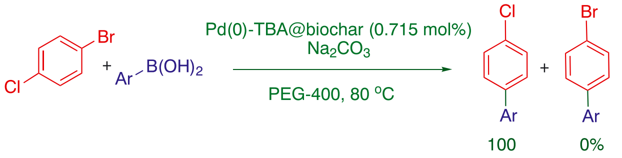
[a] Isolated yield.

3.3 | Reusability of catalyst

The reusability of Pd(0)-TBA@biochar was studied in the Suzuki coupling reaction of iodobenzene with phenylboronic acid (Figure 6a). Also, the recyclability of this catalyst was examined in the Heck reaction using the coupling of iodobenzene with butyl acrylate (Figure 6b). The obtained results for the reusability of Pd(0)-TBA@biochar in Suzuki and Heck coupling reactions are summarized in Figure 6. It was found that this catalyst can be successfully recovered for up to seven successive reaction runs. As depicted, the catalyst shows no significant change in its activity after seven runs.



SCHEME 6 Suggested mechanism for Heck reaction in the presence of Pd(0)-TBA@biochar



SCHEME 7 Selectivity in C–C coupling reaction in the presence of Pd(0)-TBA@biochar

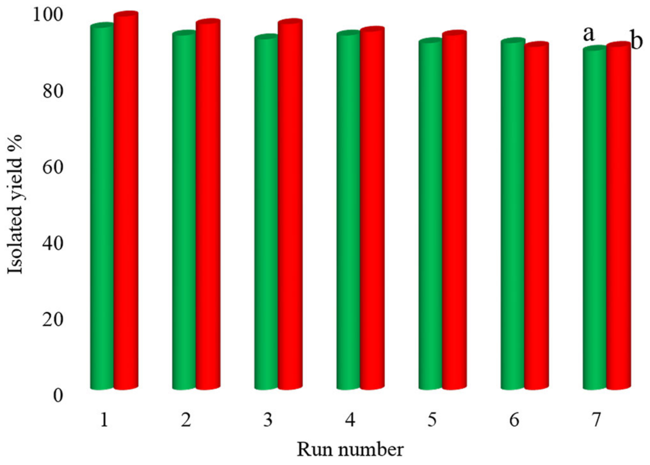


FIGURE 6 Recycling experiment of Pd(0)-TBA@biochar in (a) Suzuki reaction and (b) Heck reaction using coupling of iodobenzene with (a) phenylboronic acid and (b) butyl acrylate

3.4 | Leaching of catalyst

In order to examine the leaching of palladium from Pd(0)-TBA@biochar in the reaction mixture, poisoning test and hot filtration test were performed for the carbon–carbon coupling reaction of iodobenzene with phenylboronic acid under optimized conditions. In the hot filtration test, 59% of biphenyl was obtained in half the time of the reaction (after 63 min). In this step, the exact amount of palladium remaining in the catalyst was calculated using the AAS technique which was found to be 1.42×10^{-3} mol g^{-1}, which shows good agreement with fresh catalyst (1.43×10^{-3} mol g^{-1}). Then, the C–C coupling reaction of iodobenzene with phenylboronic acid was repeated and in half the time of the reaction, the catalyst was separated and the filtered solution was allowed to react for 125 min. In this stage, 63% of product was obtained. In this step, the recovered catalyst after 125 min was analysed using AAS, with which the exact amount of palladium was found to be 1.42×10^{-3} mol g^{-1}. As shown, the amount of palladium in the recovered catalyst shows a good agreement with fresh catalyst. These results confirmed that the leaching of palladium did not happen. Therefore, the C–C coupling reaction proceeded using heterogeneous palladium species as catalyst.

Also, the hot filtration test was performed for the Heck reaction of iodobenzene with butyl acrylate. In this experiment, in half the time of the reaction (after 35 min), 58% of butyl cinnamate was obtained. Then, the coupling of iodobenzene with butyl acrylate was repeated under optimized conditions and in half the time of the reaction, the catalyst was removed and the filtered solution was allowed to react for 70 min. In this stage, 61% of product was obtained which confirmed that the leaching of palladium did not happen.

The poisoning test is a powerful method for determining homogeneity/heterogeneity of catalysis systems. Polyvinylpyridine (PVP) poisoning and mercury poisoning tests are often employed for extinguishing solution-phase catalysis.[44–46] In order to confirm the homogeneity/heterogeneity of Pd(0)-TBA@biochar, coupling of iodobenzene with phenylboronic acid in the presence of PVP was examined. For this, a mixture of phenylboronic acid (1 mmol), iodobenzene (1.0 mmol), Na_2CO_3 (3 mmol), 0.005 g of PVP, PEG-400 (3 ml) and Pd(0)-TBA@biochar (5 mg, 0.715 mol%) was stirred at 80°C. This reaction was completed, and any changes in the reaction yield or time were not observed, which suggests that Pd(0)-TBA@biochar is heterogeneous in nature.

Results of poisoning and hot filtration tests showed good agreement for the heterogeneous nature of Pd(0)-TBA@biochar.

3.5 | Comparison of catalysts

In order to compare the activity of Pd(0)-TBA@biochar with that of previously reported catalysts, the results for the C–C coupling reaction of iodobenzene with phenylboronic acid in the presence of Pd(0)-TBA@biochar were compared with those obtained with previous catalysts (Table 5). Pd(0)-TBA@biochar is a more effective catalyst than the other catalysts. Additionally, previous catalysts require chemical

TABLE 5 Comparison of Pd(0)-TBA@biochar in the coupling reaction of iodobenzene with phenylboronic acid with previously reported procedures

Entry	Catalyst (mol%)	Reaction conditions	Time (min)	TOF (h^{-1})	Yield (%)
1	PANI-Pd (2.2 mol%)	K_2CO_3, 1,4-dioxane–H_2O (1:1), 95°C	240	10	91[60]
2	*N,N′*-Bis(2-pyridinecarboxamide)-1,2-benzene palladium complex (1 mol%)	H_2O, K_2CO_3, 100°C	180	32	97[61]
3	Pd (II)–NHC complex (1 mol%)	DMF, Cs_2CO_3, 100°C	24 h	4	99[62]
4	NHC–Pd (II) complex (1.0 mol%)	THF, Cs_2CO_3, 80°C	12 h	7	88[55]
5	Pd/Au NPs (4.0 mol %)	EtOH/H_2O, K_2CO_3, 80°C	24 h	1	88[63]
6	Pd (0)-Schiff-base@MCM-41 (1.6 mol%)	PEG, K_2CO_3, 100°C	70	50.8	95[42]
7	Pd NP (1.0 mol%)	H_2O, KOH, 100°C	12 h	4	95[64]
8	CA/Pd (0) (0.5–2.0 mol%)	H_2O, K_2CO_3, 100°C	120	94	94[65]
9	Polymer anchored Pd(II) Schiff base complex (0.5 mol%)	K_2CO_3, DMF–H_2O (1:1), 80°C	300	40	99[66]
10	Pd@SBA-15/ILDABCO (0.5 mol%)	K_2CO_3, H_2O, 80°C	90	129	97[67]
11	Pd-MPA@MCM-41 (1.7 mol%)	K_2CO_3, PEG, 100°C	120	27.94	95[47]
12	Pd(0)-TBA@biochar (0.715 mol%)	PEG-400, Na_2CO_3, 80°C	125	64	96 (this work)

procedures and chemical starting materials for their preparation which are expensive and not environmentally friendly, but biochar is made via pyrolysis of biological sources such as woody materials, agricultural wastes, green waste, animal manures and other waste products, and therefore it is inexpensive and environmentally friendly. The products were obtained in higher yields and higher TOF values in shorter reaction times when Pd(0)-TBA@biochar was used. Also application of Pd(0)-TBA@biochar as a heterogeneous catalyst was compared with homogenous catalyst in the C–C coupling reaction. The result showed that Pd(0)-TBA@biochar is more effective than homogenous catalyst in terms of reaction time and obtained yield of product (Table 5, entry 12).

4 | CONCLUSIONS

Biochar was prepared from dried chicken manure and was applied as a catalyst support for the first time. Palladium nanoparticles were supported on its surface (Pd(0)-TBA@biochar) as an efficient and reusable heterogeneous biocatalyst. Therefore, application of biochar as a catalyst support for the first time is the major novelty of this work. The presented biocatalyst was characterized using SEM, TEM, EDS, TGA, XRD and AAS, and was successfully applied for C–C coupling reactions. The present methodology offers good turnover numbers (TONs) in all reactions. Also, Suzuki and Heck coupling reactions were carried out in green solvent (PEG-400). Additionally, Pd(0)-TBA@biochar is economical and environmentally friendly as it can be recovered and reused several times.

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