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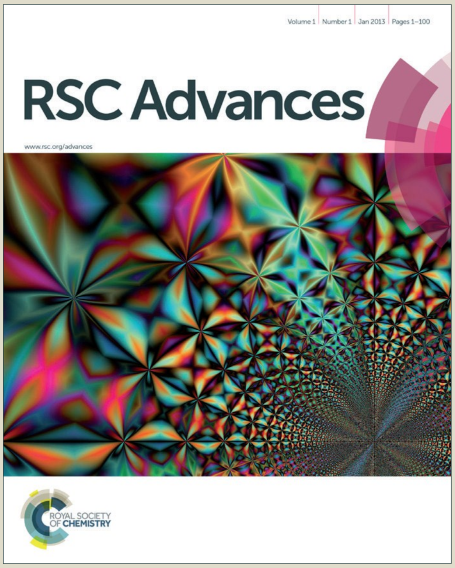

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Cite this: DOI: 10.1039/x0xx00000x

Synthesis of new Pd(0)-complex supported on boehmite nanoparticles and study of its catalytic activity for Suzuki and Heck reactions in H_2O or PEG

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Boehmite nanoparticle is a cubic orthorhombic structure of aluminum oxide hydroxide containing attached hydroxyl groups to its surface, which prepared in water using commercial available materials. A moisture- and air-stable palladium S-methylthio urea complex supported on Boehmite nanoparticles (Pd(0)-SMTU-boehmite) was prepared by very simple and inexpensive procedure without inert atmosphere using commercially available materials. This nanostructure compound was used as an excellent organometallic catalyst for the Suzuki and Heck reactions in H_2O or PEG-400. The synthesized nanoparticles were characterized by FT-IR, XRD, BET, TGA, TEM, SEM, EDS and ICP-OES techniques. Nitrogen adsorption/desorption measurement indicated that boehmite nanoparticles had BET surface area about 122.8 m^2/g. This heterogeneous nanocatalyst was easily separated from the reaction mixture and reused for several consecutive runs without significant loss of its catalytic efficiency or palladium leaching. The leaching of palladium from catalyst has been examined by hot filtration and ICP-OES techniques.

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1 Introduction

Boehmite is an aluminum oxide hydroxide (γ-AlOOH) particles, which the surface of boehmite nanoparticles covered with hydroxyl groups. Boehmite is structure consists of double sheets of octahedral with aluminum ions at their centers and the sheets themselves are composed of octahedral chains and has a cubic orthorhombic structure. Also, boehmite nanoparticles was not moisture-or air sensitive, and was synthesized in H_2O at room temperature without inert atmosphere using available materials such as $Al(NO_3)_3.9H_2O$ and NaOH. Boehmite has important applications in the preparation of catalysts in petrochemical and petroleum refining processes [1]. Boehmite is an important precursor material for the preparation of ceramic membranes and coatings [1-3]. Boehmite is also used for building units and directing template in the preparation of core/shell materials [2], which has been extensively used as catalyst, optical material, cosmetic products, vaccine adjuvants, pillared clays and sweep-flocculation for fresh water treatment and adsorbent [2-4], due to its unique properties such as good porosity and thermal stability, high specific surface area (>120 m^2/g) [5, 6]. Another important application of boehmite is producing α-Al_2O_3 by calcinations at high temperatures [6]. Furthermore, boehmite has excellent properties such as chemical resistance, good mechanical strength, good conductivity, high hardness, transparency, low cost, high abrasive and corrosion resistance, excellent biocompatibility, relatively and controllable synthesis [7, 8]. The chemical and physical properties of boehmite nanoparticles are very dependent on the experimental factors of its synthesis, such as the nature of Al(III)-salt, pH, temperature, time of aging and etc. Therefore, numerous methods have been reported for the preparation of boehmite nanoparticles such as hydrothermal (HS) [9], sol–gel [10], and hydrolysis of aluminum [11]. Also effect of temperature, ultrasonic waves, time and Al/OH molar ratio on the synthesis of boehmite has been studied by L. Rajabi et al. [4]. Despite several studies on morphology, properties and preparation of boehmite, there are few reports on the modification of nano boehmite surface that have been reported as heterogeneous catalyst [12-14]. Therefore, an attempt has been made to modify surface of boehmite nanoparticles in this work. In this regards, palladium S-methylthio urea complex has been supported on boehmite nanoparticles and applied as an excellent and reusable nano organometallic catalyst for the C-C coupling reactions, because cross-coupling reactions were used as a powerful method in modern synthetic organic chemistry for the preparation of natural products, advanced materials, agrochemicals, pharmaceuticals, herbicides, biologically active compounds, polymers, UV screens, preparation of hydrocarbons and liquid crystal materials [15-19].

2 Results and discussion

2.1 Catalyst preparation

In continuation of our studies on the application of immobilized metal complex on boehmite nanoparticles in organic reactions [3, 12], herein, we report the preparation and characterization of Pd(0) complex supported on Boehmite nanoparticles. Initially, the nano Boehmite has been prepared *via* addition of NaOH to the solution of $Al(NO_3)_3.9H_2O$ as source of aluminum at room temperature. Subsequently, boehmite nanoparticles were modified with 3-chloropropyltrimethoxysilane (CPTMS) then grafting of S-methylisothiourea (SMTU) on the prepared nPr-Cl-boehmite achieve S-methylisothiourea-functionalized boehmite nanoparticles (SMTU-boehmite). Finally Pd nanoparticles have been supported on SMTU-boehmite (Pd(0)-SMTU-boehmite) by the concise route that outlined in Scheme 1.

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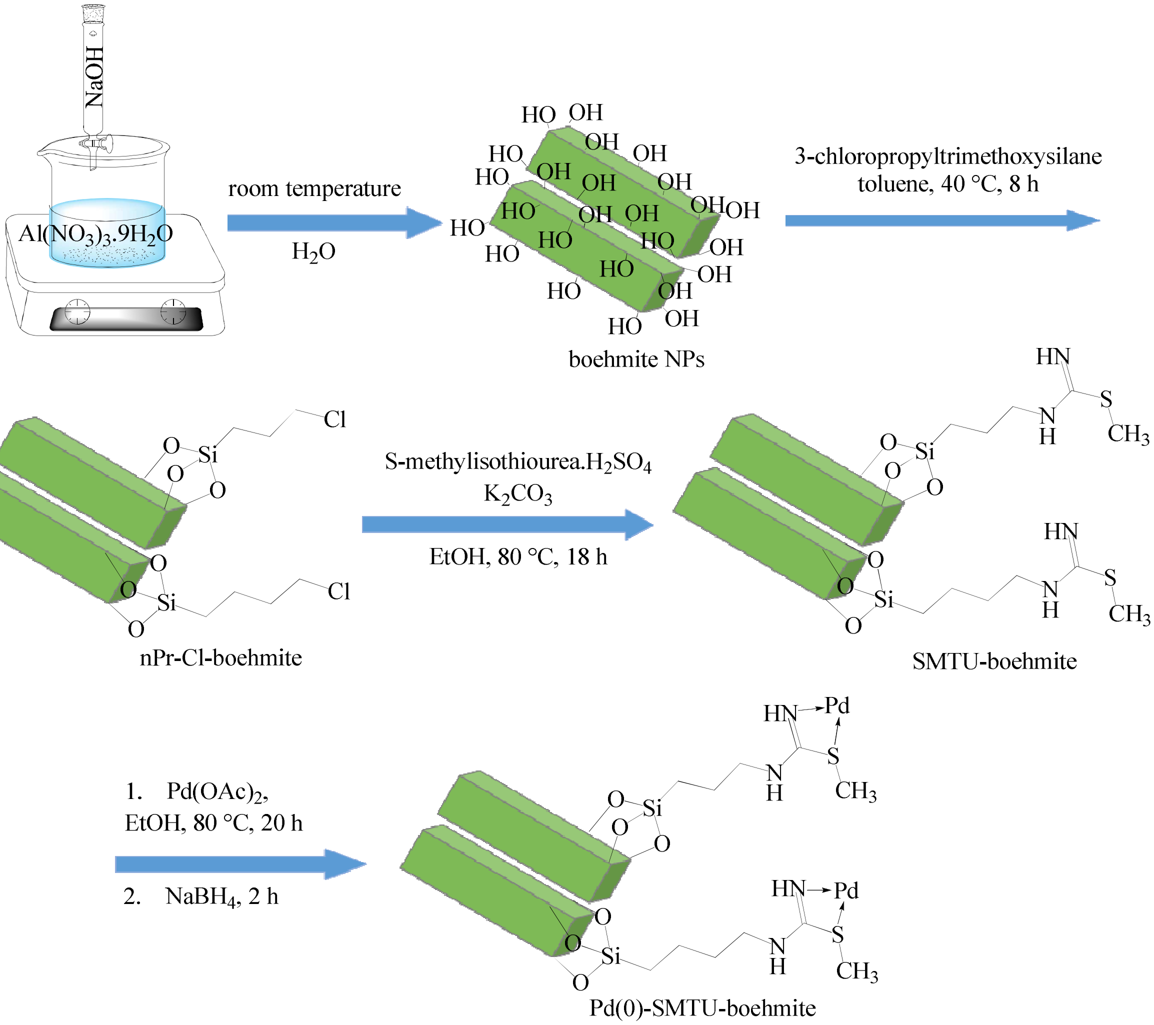

Scheme 1. Synthesis of Pd(0)-SMTU-boehmite.

2.2 Catalyst characterizations

The prepared nanoparticles have been characterized by SEM, TEM, EDS, TGA, XRD, BET, FT-IR and ICP-OES techniques.
The XRD patterns of boehmite nanoparticles and Pd(0)-SMTU-boehmite are shown in Figure 1. As it can be seen in Figure 1, the boehmite phase was characterized by the peak positions at the 2θ values of 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 could be attributed for the (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. This XRD patterns of boehmite nanoparticles is conforming to the standard boehmite nanoparticles XRD spectrum and the all peaks can be confirmed the crystallization of boehmite with an orthorhombic unit cell [14, 20]. Also the XRD pattern of Pd(0)-SMTU-boehmite contains a series of peaks (39°, 46° and 67°) which are indexed to the Pd (0) on the surface of boehmite [21-24], which they have overlapped with 0 3 1, 1 3 1, 2 3 1, 0 0 2 and 1 7 1 reflections.

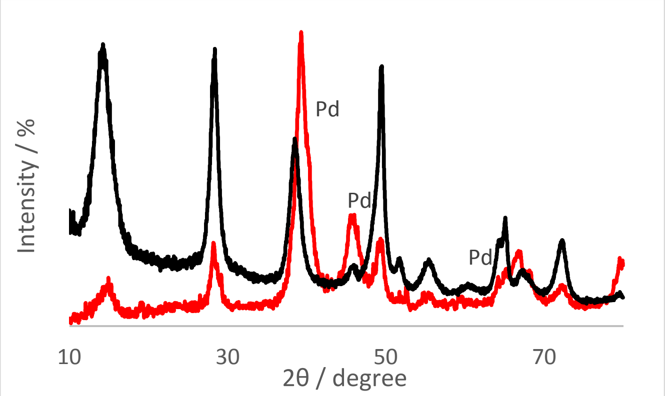

Figure 1. The XRD pattern of boehmite nanoparticles (black line) and Pd(0)-SMTU-boehmite (red line).

Figure 2 shows the FT-IR spectrums of boehmite, nPr-Cl-boehmite, SMTU-boehmite and Pd(0)-SMTU-boehmite. The FT-IR spectrum of the boehmite nanoparticles (Spectrum a) shows two strong bands at 3086 and 3308 cm^{-1}, which are attributed to the both symmetrical and asymmetrical modes of the O-H bonds on the surface of boehmite nanoparticles [3, 14]. In FT-IR Spectrums a-d, several peaks that appear at 480, 605 and 735 cm^{-1} can be related to the absorption of Al-O bonds [12]. Also, the nitrate impurity vibration at 1650 cm^{-1} and the vibrations of hydrogen bands OH…OH by two strong absorption bands at 1164 and 1069 cm^{-1} were observed in FT-IR spectrum [3, 4]. In the FT-IR spectra of nPr-Cl-boehmite (Spectrum b), The presence of the anchored chloropropyltrimethoxysilane is confirmed by C–H stretching vibrations that appears at 2955 cm^{-1} and also O-Si stretching vibration modes that appear at 1073 cm^{-1} [26]. In the FT-IR spectra of SMTU-boehmite (Spectrum c), the existence of the grafted S-methylisothiourea groups is identified by C=N vibrations that appear at 1638 cm^{-1}, which this band has been shifted to lower frequency (1631 cm^{-1}) in the catalyst (Spectrum d), which indicates the formation of palladium complex on surface of functionalized nano boehmite [27].

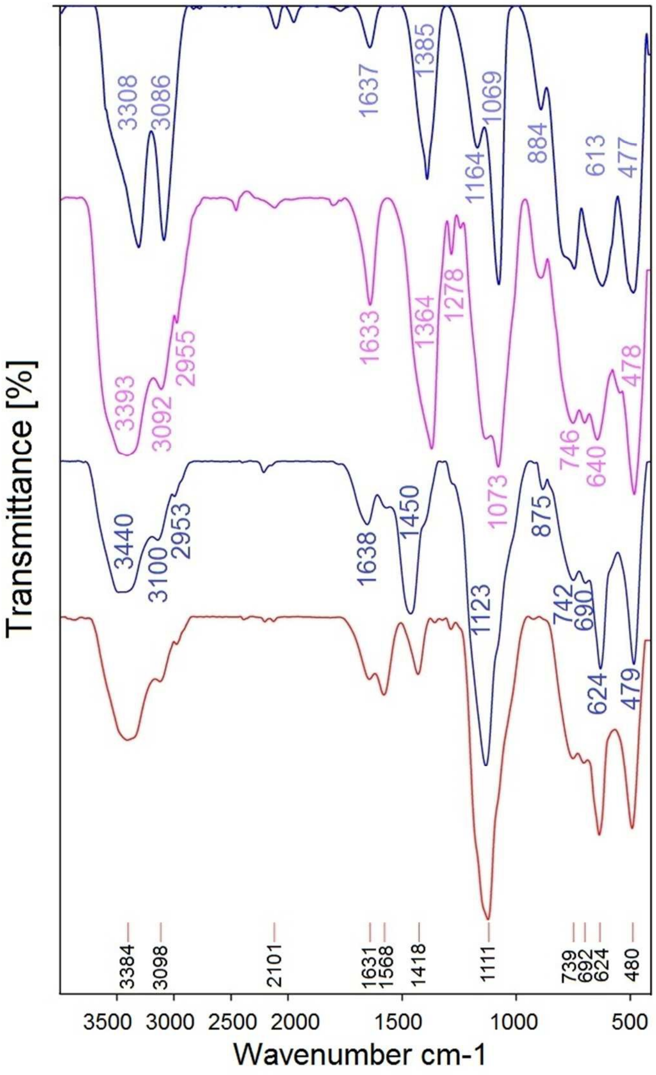

Figure 2. FT-IR spectra of (a) boehmite, (b) nPr-Cl-boehmite, (c) SMTU-boehmite and (d) Pd(0)-SMTU-boehmite.

The orthorhombic structure of boehmite nanoparticles was confirmed by SEM (Figure 4) technique. TEM image (Figure 3) revealed more accurate information on the morphology and particles size of the palladium nanoparticles. It can be seen that most of the palladium nanoparticles are in nano size with an average diameter about 5-10 nm.

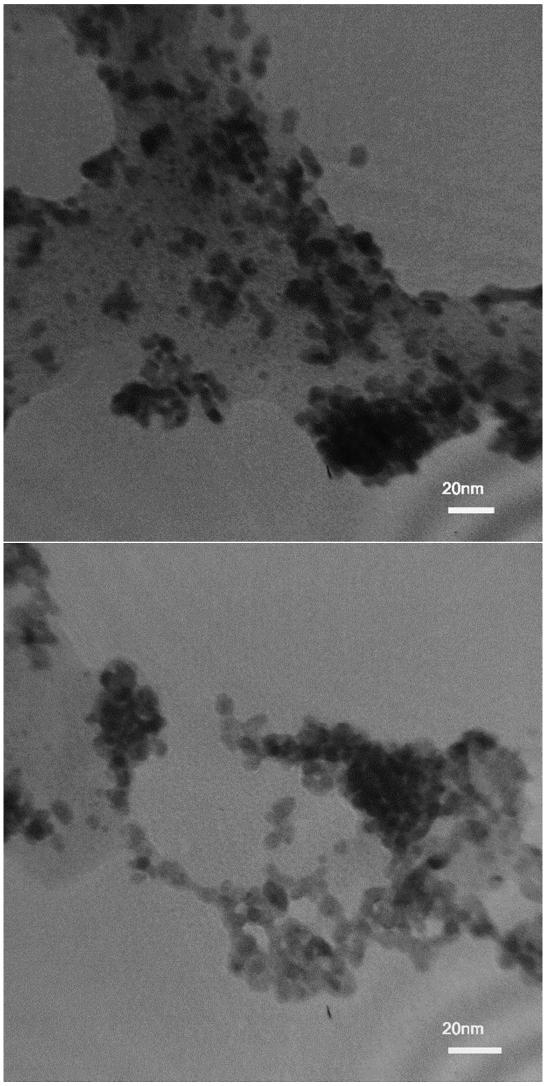

Figure 3. TEM images of Pd(0)-SMTU-boehmite.

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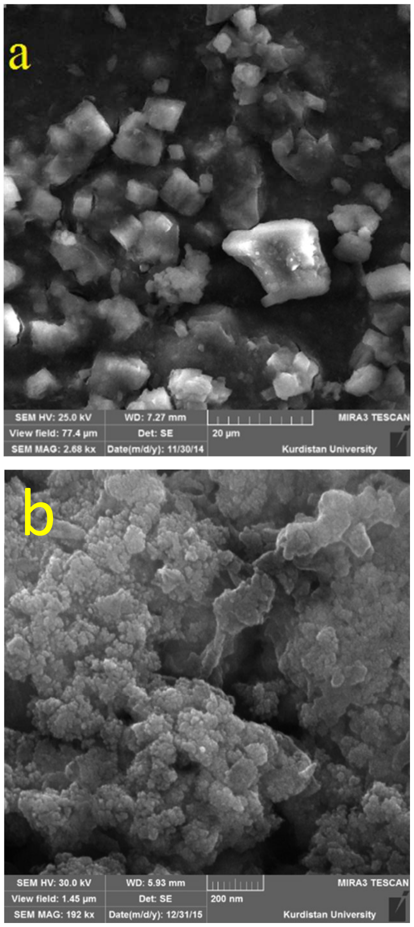

Figure 4. SEM images of boehmite (a) and Pd(0)-SMTU-boehmite (b).

In order to prove the presence of palladium metal on the surface of functionalized boehmite, EDS technique has been applied. The EDS spectrum of Pd(0)-SMTU-boehmite was shown in Figure 5. As shown in Figure 5, EDS spectrum of Pd(0)-SMTU-boehmite shows the presence of Al, O, Si, C, S, N and as well as Pd species in Pd(0)-SMTU-boehmite. Also for quantitative analysis and find out the exact amount of palladium, ICP-OES has been applied. According to the inductively coupled plasma (ICP) analysis, the exact amount of palladium in the heterogeneous catalyst has been calculated that it to be 2.55 mmol g^{-1}.

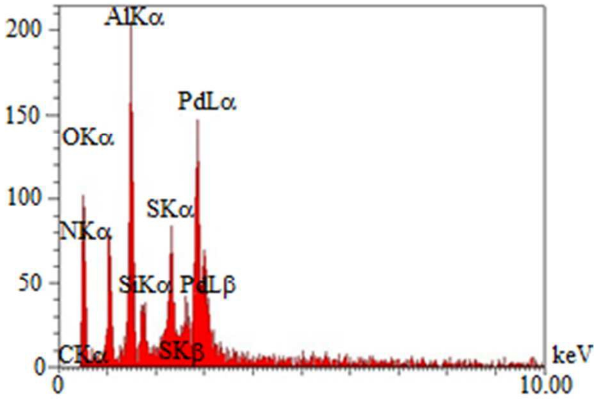

Figure 5. EDS spectrum of Pd(0)-SMTU-boehmite.

The nitrogen adsorption-desorption isotherms of boehmite nanoparticles is shown in Figure 6. The N_2 physical adsorption and desorption isotherms were adopted at 120 °C to obtain surface areas, which the Brunauer–Emmett–Teller (BET) surface area for boehmite nanoparticles was obtained in 122.8 m^2/g. When the Pd complex loaded on boehmite nanoparticles, the BET specific surface areas decreased from 122.8 to 82.90 m^2/g. As shown in Table 1, BET analysis of boehmite nanoparticles shows a pore diameter of 1.64 nm and a pore volume of 0.22 cm^3/g.

The pore volume and pore diameter of Pd(0)-SMTU-boehmite is lower than boehmite nanoparticles. On the basis of these results, the well grafting of organic groups including palladium on the boehmite nanoparticles is verified.

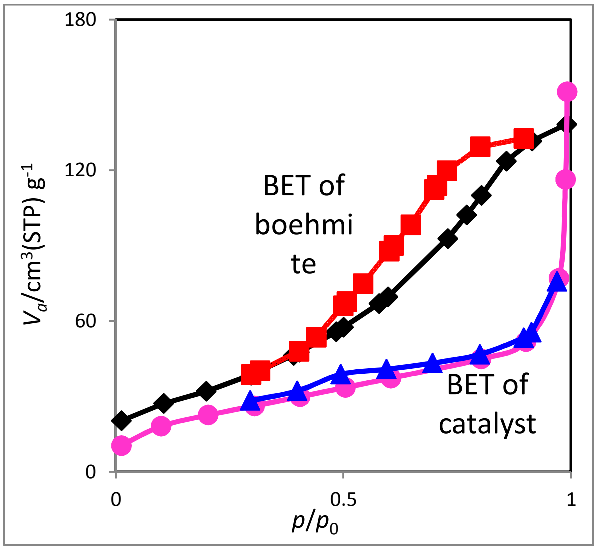

Figure 6. Nitrogen adsorption–desorption isotherms of boehmite nanoparticles and Pd(0)-SMTU-boehmite.

Table 1. Textural parameters deduced from nitrogen sorption isotherms of boehmite nanoparticles and Pd(0)-SMTU-boehmite

sample	S_{BET} (m^2/g)	Pore diam. By BJH method (nm)	Pore vol. (cm^3/g)
boehmite nanoparticles	122.8	1.64	0.22
Pd(0)-SMTU-boehmite	82.90	1.21	0.19

Figure 7 shows the TGA analysis of boehmite nanoparticles, SMTU-boehmite and Pd(0)-SMTU-boehmite. The results were confirmed by TGA analysis data by showing 16% weight loss from 25-250 °C for nano boehmite, which is due to desorption of water and dehydration of surface hydroxyl groups [25]. The total mass loss of the SMTU-boehmite was approximately 29% from 300-800 °C, which is attributed to the decomposition of immobilized organic moieties on the nano boehmite surface. Meanwhile, weight loss about 40% from 250 to 800 °C is occurred for Pd(0)-SMTU-boehmite. On the basis of these results, the well grafting of organic groups including palladium complex on the boehmite nanoparticles is verified.

Thermal stability of the Pd(0)-SMTU-boehmite was also considered. As shown in Figure 6, this catalyst was stable even at 300 ºC.

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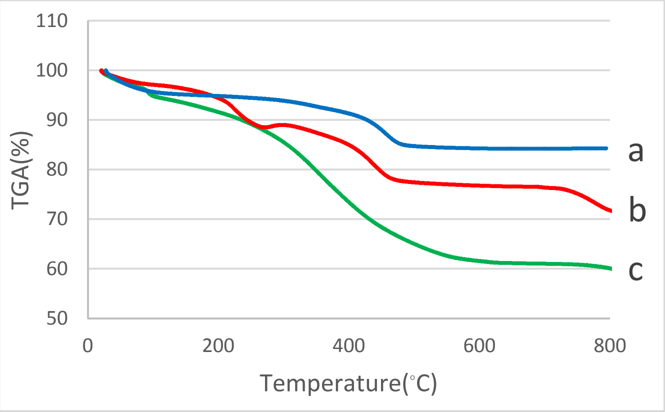
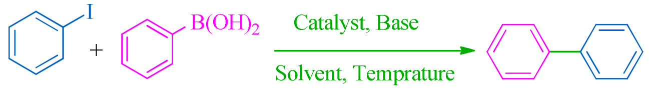


Figure 7. TGA diagram of boehmite (a), SMTU-boehmite (b) and Pd(0)-SMTU-boehmite (c).

2.3 Catalytic activity of Pd(0)-SMTU-boehmite in the C-C coupling reactions

Cross-coupling reactions such as Suzuki and Heck reactions are powerful tools for the preparation of natural products, advanced materials, agrochemicals, pharmaceuticals and biologically active compounds [28-37]. Therefore, we investigated catalytic activity of Pd(0)-SMTU-boehmite as a new heterogeneous and high reusable nanocatalyst for the C-C coupling through Suzuki reaction. For this purpose, the coupling of iodobenzene with phenylboronic acid has been selected as a simple model reaction to establish the feasibility of the strategy and optimize the reaction conditions, and the results are summarized in Table 2. We examined the effect of different parameters (including solvent, base, reaction temperature, and amounts of Pd(0)-SMTU-boehmite) on the outcome of C-C coupling reaction of iodobenzene with phenylboronic acid (Table 2). The catalyst is not thermal, air, or moisture sensitive and hence inert atmosphere was not employed in all reactions. Interestingly, the reaction did not proceed in the absence of Pd(0)-SMTU-boehmite even after 6 hour (Table 2, entry 1). In order to choose the reaction media, different solvents such as PEG, DMF, DMSO, H_2O and ethanol were used (Table 1, entries 5-9) and the best result was obtained in H_2O in the presence of 0.005 gr (0.8 mol%) of Pd(0)-SMTU-boehmite (Table 2, entry 14). Also, the effect of nature and amount of base was studied, which inferior results were obtained using NaOEt, KOH, and Et_3N (Table 1, entries 9-11). Excellent biphenyl yields were obtained using 1.5 mmol of sodium carbonate at room temperature. As shown in Table 2, iodobenzene (1 mmol) in the presence of catalytic amount of Pd(0)-SMTU-boehmite (0.005 g, 0.8 mol%) and Na_2CO_3 (1.5 mmol) reacted with phenylboronic acid (1 mmol) in H_2O at room temperature as ideal reaction conditions for the formation of corresponding biphenyl.

Table 2. Optimization of reaction conditions for the C-C coupling reaction of iodobenzene with phenylboronic acid in the presence of Pd(0)-SMTU-boehmite



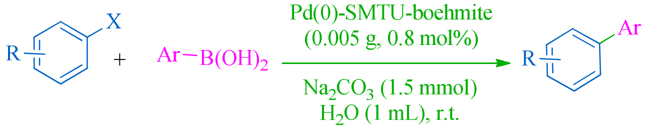
Entry	Catalyst (mg)	Solvent	Base	Amount of base (mmol)	Temperature (ºC)	Time (min)	Yield (%)[a]
1	-	H_2O	Na_2CO_3	3	80	360	-[b]
2	3	H_2O	Na_2CO_3	3	80	35	85
3	5	H_2O	Na_2CO_3	3	80	25	90
4	7	H_2O	Na_2CO_3	3	80	20	91
5	5	PEG	Na_2CO_3	3	80	25	88
6	5	EtOH	Na_2CO_3	3	80	25	70
7	5	DMSO	Na_2CO_3	3	80	25	22
8	5	DMF	Na_2CO_3	3	80	25	15
9	5	H_2O	NaOEt	3	80	25	10
10	5	H_2O	Et_3N	3	80	25	15
11	5	H_2O	KOH	3	80	25	32
12	5	H_2O	Na_2CO_3	1.5	80	30	90
13	5	H_2O	Na_2CO_3	1.5	60	40	93
14	5	H_2O	Na_2CO_3	1.5	r.t.	45	94

[a] Isolated yield, [b] No reaction.

After the optimization of the reaction conditions, we examined the catalytic activity of Pd(0)-SMTU-boehmite for various substrates and the results are shown in Table 3. Various aryl iodides (Table 3, entries 1, 2 and 12), bromides (Table 3, entries 3-8, 13 and 14) and chlorides (Table 3, entries 9-11) were converted into corresponding biphenyls. However, the completing reaction including aryl chlorides was slower than aryl iodides and bromides. The aryl halides including electron-donor and electron-withdrawing functional groups have been successfully converted to corresponding biphenyls in short reaction times with good to excellent yields (Table 3). Therefore, the experimental procedure is very simple and convenient, and has the ability to tolerate a variety of different functional groups such as OH, CN, NO_2, alkyl and OCH_3 under the reaction conditions.

We also applied optimized reaction conditions to coupling of aryl halides with 3,4-difluoro phenylboronic acid. However, 3,4-difluoro phenylboronic acid showed less reactivity toward the coupling reaction than unfunctionalized phenylboronic acid. In this aim, iodobenzene, bromobenzene and 4-nitrobromobenzene reacted with 3,4-difluoro phenylboronic acid and the corresponding cross-coupling products was obtained in the reasonable yields (Table 3, entries 13-15). Therefore, these results revealed that this methodology is effective for a wide range of aryl halides and phenylboronic acid deriavatives.

Table 3. Catalytic C-C coupling reaction of aryl halides using phenylboronic acid or 3,4-difluoro phenylboronic acid in the presence of Pd(0)-SMTU-boehmite (0.005 g, 0.8 mol%) under optimized conditions.



Entry	Aryl halide	Ar-B(OH)$_2$	Time (min)	Yield (%)[a]	Melting point (ºC) [Ref.]	Reported melting point (ºC) [Ref.]
1	Iodobenzene	$C_6H_5B(OH)_2$	45	94	68	67-68 [17]
2	4-Iodotoluene	$C_6H_5B(OH)_2$	90	87	45-46	44-47 [17]
3	Bromobenzene	$C_6H_5B(OH)_2$	90	92	66-68	67-68 [17]
4	4-Bromotoluene	$C_6H_5B(OH)_2$	180	85	44-46	44-47 [17]
5	4-Bromobenzonitrile	$C_6H_5B(OH)_2$	50	90	86-88	83 [21]

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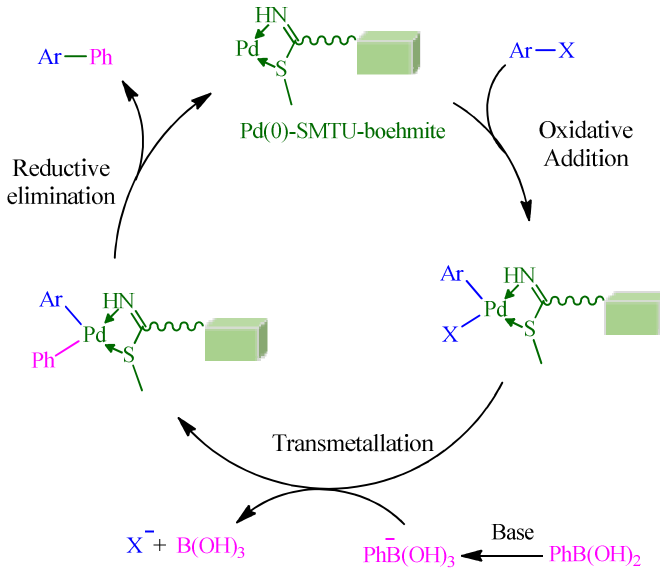
6	4-Bromonitrobenzene	$C_6H_5B(OH)_2$	25	99	110-113	111-113 [21]
7	4-Bromophenol	$C_6H_5B(OH)_2$	90	96	157-160	157-160 [21]
8	4-Bromochlorobenzene	$C_6H_5B(OH)_2$	90	98	69-71	70-71 [17]
9	Chlorobenzene	$C_6H_5B(OH)_2$	185	93	67-69	67-68 [17]
10	4-Chloronitrobenzene	$C_6H_5B(OH)_2$	50	93	111-114	111-113 [21]
11	4-Chlorobenzonitrile	$C_6H_5B(OH)_2$	90	97	87-89	83 [21]
12	Iodobenzene	3,4-diF-$C_6H_5B(OH)_2$	360	89	39-41	-
13	Bromobenzene	3,4-diF-$C_6H_5B(OH)_2$	420	91	40-42	-
14	4-Bromonitrobenzene	3,4-diF-$C_6H_5B(OH)_2$	390	98	119-120	-

^{a} Isolated yield

Catalytic cycle for this C–C bond formation reaction in the presence of Pd(0)-SMTU-boehmite was outlined in Scheme 2 [38, 39].



Scheme 2. Mechanism of the Pd(0)-SMTU-boehmite-catalyzed Suzuki reaction.

In order to extend applications of the catalytic activity of Pd(0)-SMTU-boehmite, this catalyst was investigated in the C-C coupling through Heck reaction. The Pd(0)-SMTU-boehmite has been tested as heterogeneous catalyst in the cross-coupling of iodobenzene with butyl acrylate to ascertain the best conditions reaction. The effect of solvent (DMF, DMSO, H_2O, EtOH or PEG), temperature (room temperature to 120 °C), amounts of catalyst, nature and amount of base (Et_3N, Na_2CO_3, KOH or NaOEt) on the outcome of the coupling of iodobenzene with butyl acrylate were examined. A summary of the results is shown in Table 4. The reaction did not perform in the absence of Pd(0)-SMTU-boehmite (Table 4, entries 4 and 10). Among of different solvents, the best results were obtained in PEG using 0.016 g (2.56 mol%) of Pd(0)-SMTU-boehmite (Table 4, entry 4). Also, the reaction was significantly affected by the nature and amount of base. Therefore, to found the best reaction conditions, the effect and amount of base was described (Table 4, entries 8-11) and the best results were obtained using 1.5 mmol of Na_2CO_3. Becase, the coupling reaction yields were susceptible to temperature changes. Therefore, to found the best reaction conditions, different bases was examined in model reaction (Table 4, entries 11-14). As shown in Table 4, the best result was obtained with Na_2CO_3 (1.5 mmol) in the presence of 16 mg (2.56 mol%) of Pd(0)-SMTU-boehmite in PEG-400 as solvent at 120 °C (inferior results were observed at 80 and 100 °C).

Table 4. Optimization of reaction conditions for the C-C coupling reaction of iodobenzene with butyl acrylate

Entry	Catalyst (mg)	Solvent	Base	Amounts of base (mmol)	Temperature (ºC)	Time (min)	Yield (%)^a
1	-	PEG	Na_2CO_3	3	120	360	-^{b}
2	10	PEG	Na_2CO_3	3	120	80	92
3	12	PEG	Na_2CO_3	3	120	50	90
4	16	PEG	Na_2CO_3	3	120	15	95
5	16	H_2O	Na_2CO_3	3	120	15	Trace
6	16	DMSO	Na_2CO_3	3	120	15	64
7	16	EtOH	Na_2CO_3	3	120	15	80
8	16	PEG	NaOEt	3	120	15	Trace

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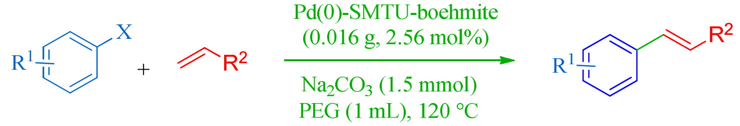
9	16	PEG	Et_3N	3	120	10	96
10	16	PEG	KOH	3	120	20	41
11	16	PEG	Na_2CO_3	1.5	120	20	97
12	16	PEG	Na_2CO_3	1.5	100	20	80
13	16	PEG	Na_2CO_3	1.5	80	20	65
14	16	PEG	Na_2CO_3	1.5	r.t.	20	15

[a] Isolated yield.

After the optimization of the reaction conditions, we extended the catalytic activity of Pd(0)-SMTU-boehmite for other substrates and the results are summarized in Table 5. Therefore, optimized reaction conditions was applied to wide range of aryl iodides (Table 5, entries 1-3 and 13-15), bromides (Table 5, entries 4-8 and 12) and chlorides (Table 5, entries 9-11) using butyl acrylate under the optimized reaction conditions. Aryl bromides and aryl iodides need less reaction times compared to those corresponding aryl chlorides (Table 5, entries 9-11 and 13). As shown in Table 5, this methodology is applicable for wide range of aryl halides with electron-donor and electron-withdrawing functional groups that reacted with butyl acrylate to afford the corresponding products and the all products were obtained in good to excellent yields.

We also applied optimized reaction conditions to coupling aryl halides with acrylonitrile (Table 5, entries 11-15). The aryl iodides, bromides and chlorides reacted with acrylonitrile to produce the corresponding cross-coupling products in good to excellent yields. However, acrylonitrile showed high reactivity toward the coupling reaction than butyl acrylate. Therefore, these results revealed that this methodology is effective for a wide range of alkenes and aryl halides.

Table 5. Coupling of aryl halides with butyl acrylate or acrylonitrile in the presence of catalytic amounts of Pd(0)-SMTU-boehmite (16 mg, 2.56 mol%).



Entry	Aryl halide	Alkene	Time (min)	Yield (%)[a]
1	Iodobenzene	Butyl acrylate	20	97
2	4-Iodotoluene	Butyl acrylate	270	96
3	4-Iodoanisole	Butyl acrylate	260	93
4	4-Bromotoluene	Butyl acrylate	16.5 h	91
5	4-Bromoanisole	Butyl acrylate	12 h	96
6	4-Bromophenol	Butyl acrylate	17 h	89
7	Bromobenzene	Butyl acrylate	8 h	93
8	1-Bromo-3-(trifluoromethyl)benzene	Butyl acrylate	3 h	88
9	Chlorobenzene	Butyl acrylate	16 h	88
10	4-Chlorophenol	Butyl acrylate	24h	94
11	Chlorobenzene	Acrylonitrile	300	93
12	Bromobenzene	Acrylonitrile	150	96
13	Iodobenzene	Acrylonitrile	60	94
14	4-Iodoanisole	Acrylonitrile	215	88
15	4-Iodotoluene	Acrylonitrile	180	90

[a] Isolated yield.

The formation of the products through Heck reaction can be explained by a plausible mechanism as shown in Scheme 3. As shown in Scheme 3, the full catalytic cycle involves oxidative addition, migratory insertion, beta-hydride elimination and reductive elimination [40-42].

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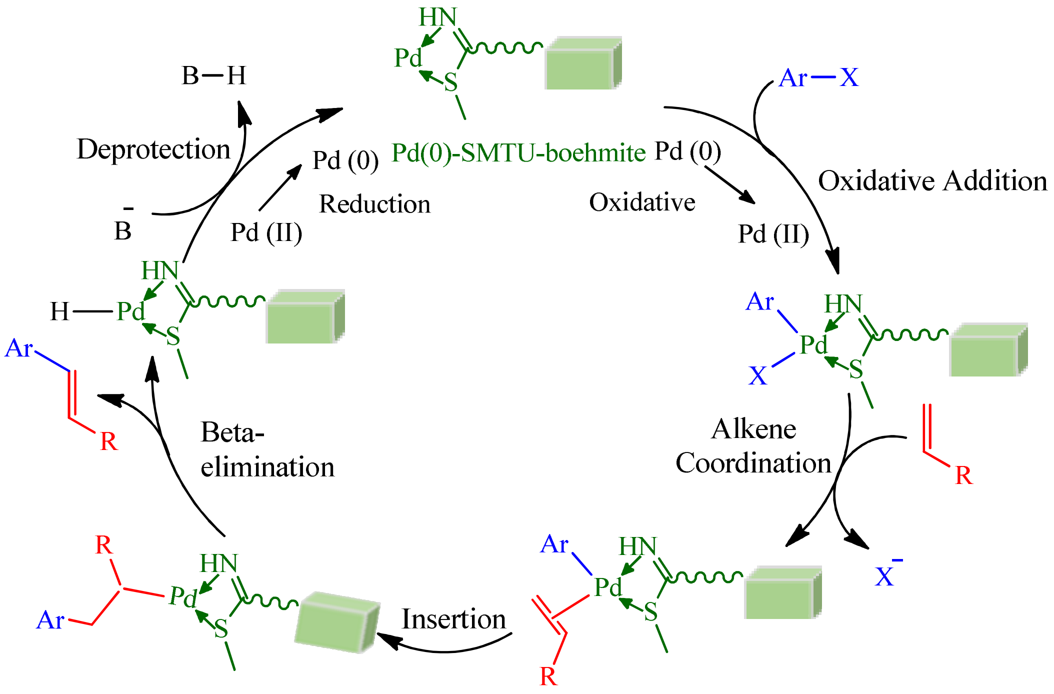

Scheme 3. Mechanism of the Pd(0)-SMTU-boehmite-catalyzed Heck reaction.

In order to show the efficiency of described catalytic system, the obtained results for the model compounds in this project was compared with previously reported procedures in the literature. Comparison of the results shows a better catalytic activity of Pd(0)-SMTU-boehmite in Suzuki reaction (Table 6). As shown in Table 6, many catalysts have been reported for the Carbon-Carbon coupling reactions that most of them have some drawbacks or limitations such as use of homogeneous catalysts that is difficult to separate catalyst from the reaction mixture, using excess of catalyst or phenylboronic acid, hazardous organic solvents, high temperature and long reaction times. Meanwhile, in this work, C-C bond forming through Suzuki reaction has been carried out in water at room temperature with short reaction times. Also this new catalyst is comparable with previously reported catalysts in terms of price, non-toxicity, stability and easy separation. Moreover, the mesoporous silica such as MCM-41, SBA-15 or some nanoparticles such as TiO_2 NPs, which have been used as catalyst supports in the organic reactions, requires high temperature for calcination and a lot of time and tedious conditions to prepare. Also some of previously reported catalysts such as heteropolyacids, ionic liquids or some polymers are more expensive. Also, some of heterogeneous supports such as Fe_3O_4 nanoparticles require inert atmosphere and tedious conditions to prepare. Meanwhile, preparation of boehmite nanoparticles was not air, or moisture sensitive, therefore this nanomaterial was prepared in water at room temperature without inert atmosphere. Here, we used the Pd(0)-SMTU-boehmite catalyst that have advantages of air or moisture stable, ease of preparation and catalyst recycling without significant loss of catalytic activity (Figure 8). As shown in Figure 6, the catalyst can be reused over 5 times in the coupling of iodobenzene with phenylboronic acid or coupling of 4-iodotoluene with butyl acrylate without any significant loss of its catalytic activity or palladium leaching. The average isolated yield for 5 successive cycles in Suzuki and Heck reactions were 96 % and 92.6% respectively, which clearly demonstrates the practical recyclability of this catalyst. Metal leaching of the catalyst was studied by hot filtration test and ICP analysis. Based on the results from ICP-OES analysis, the amount of palladium in fresh catalyst and the recovered catalyst after 5 runs were 1.64 mmol g^{-1} and 1.62 mmol g^{-1}, respectively, which indicated that Pd leaching of the catalyst was very low. In order to examine leaching of palladium in reaction mixture and heterogeneity of described catalyst, we performed hot filtration in the Heck reaction through coupling of iodobenzene and butyl acrylate. In this study we found the yield of product in the half time of the reaction was 55%. Then the reaction was repeated and in half time of the reaction, the catalyst separated and allowed the filtrate to react further. The yield of reaction in this stage was 58% that confirmed the leaching of palladium hasn't been occurred.

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

Entry	Catalyst (mol% of Pd)	Condition	Time (min)	Yield (%)[a]	Ref.
1	Polymer anchored Pd(II) Schiff base complex (0.5 mol%)	K_2CO_3, DMF: H_2O (1:1), 80 ºC	5h	99	[15]
2	Fe_3O_4/SiO_2–DTZ–Pd (0.5 mol %)	Na_2CO_3, PEG, 60 ºC	130	94	[17]
3	Pd@SBA-15/ILDABCO (0.5 mol%)	K_2CO_3, H_2O, 80 ºC	90	97	[28]
4	SBA-16-2 N-Pd(II) (0.5 mol%)	EtOH, K_2CO_3, 60 ºC	120	99	[29]
5	NHC-Pd(II) complex (1.0 mol%)	THF, Cs_2CO_3, 80 ºC	12h	88	[30]
6	Pd NP (1.0 mol%)	H_2O, KOH, 100 ºC	12 h	95	[31]
7	CA/Pd(0) (0.5-2.0 mol%)	H_2O, K_2CO_3, 100 ºC	120	94	[32]

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8	$PdCl_2$ (0.05 mol%)	DMF, Cs_2CO_3, 130 ºC	120	95	[33]
9	Pd/Au NPs (4.0 mol%)	EtOH/H_2O, K_2CO_3, 80 ºC	24h	88	[34]
10	Pd-MPTAT-1 (0.02 g)	NaOH, DMF: H_2O (1:5), 85 ºC	8h	95	[35]
11	LDH-Pd(0) (0.3 g)	K_2CO_3, 1,4-dioxane: H_2O (5:1), 80 ºC	10h	96	[36]
12	PANI-Pd (2.2 mol%)	K_2CO_3, 1,4-dioxane: H_2O (1:1), 95 ºC	4h	91	[37]
13	Pd-SMTU-boehmite (0.8 mol%)	H_2O, Na_2CO_3, room temperature	45	94	This work
14	Pd(0)-SMTU-boehmite (0.32 mol%)	H_2O, Na_2CO_3, 80 ºC	75	95	This work

[a] Isolated yield

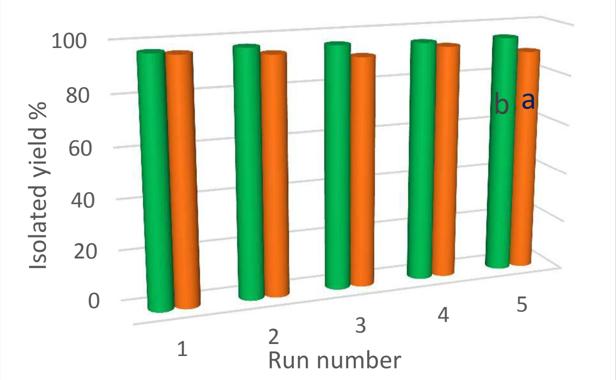

Fig 8. Recyclability of Pd(0)-SMTU-boehmite in the coupling of iodobenzene with phenylboronic acid (a) and coupling of 4-iodotoluene with butyl acrylate (b).

In order to show the structure stability of catalyst after recycling, recovered catalyst has been characterized by FT-IR and XRD techniques. The recovered catalyst was investigated by XRD pattern (Figure 9) and FT-IR (Figure 10). FT-IR and XRD pattern of recovered Pd(0)-SMTU-boehmite indicates that this catalyst can be recycled without any change in its structure.

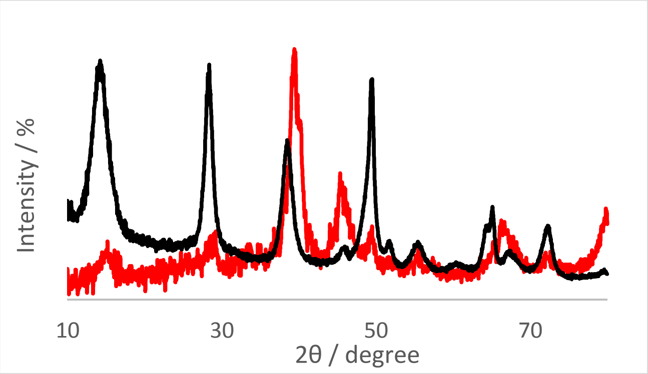

Figure 9. The XRD pattern of boehmite nanoparticles (black line) and Pd(0)-SMTU-boehmite after 10 runs recycling (red line).

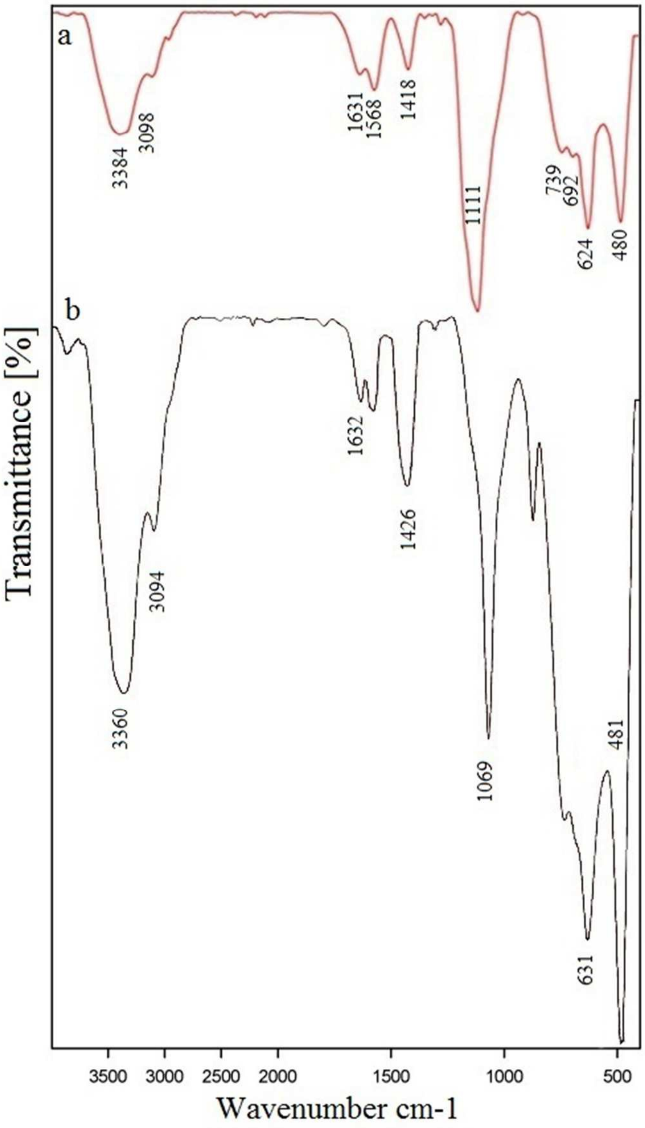

Figure 10. FT-IR spectra of (a) fresh Pd(0)-SMTU-boehmite and recovered Pd(0)-SMTU-boehmite (b).

3 Conclusions

In summary, a novel type of boehmite-recoverable nanocatalyst (Pd(0)-SMTU-boehmite) was synthesized from immobilization of Pd nanoparticles on functionalized boehmite nanoparticles. This catalyst showed excellent catalytic activity, high reusability and air or moisture stability for the Heck and Suzuki reactions in water or PEG-400. The advantages of this protocol are the use of a

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commercially available, eco-friendly, cheap, chemically stable materials, the operational simplicity, practicability and good to high yields, and more importance the catalyst can be synthesized readily from inexpensive and commercially available starting materials. Also, nano boehmite is new support for heterogenization of homogeneous catalysts, which prepared by very simple procedure in water at room temperature using commercially available materials. The catalyst can be reused for 5 times without Pd leaching or any significant loss of its activity.

4 Experimental

4.1. Material

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°/min 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). Nitrogen adsorption/desorption isotherms were recorded at 120 °C with a Brunauer Emmett Teller Analysis Adsorption BELSORP Mini II. IR spectra were recorded as KBr pellets on a VRTEX 70 model BRUKER FT-IR spectrophotometer. The content of Pd was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES). ^{1}H NMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 MHz. Melting points were measured with an Electrothermal 9100 apparatus.

4.2 Preparation of catalyst

The solutions of NaOH (6.490 g) in 50 mL of distilled water was added to solutions of $Al(NO_3)_3.9H_2O$ (20 g) in 30 mL distilled water as drop to drop under vigorous stirring. The resulting milky mixture was subjected to mixing in the ultrasonic bath for 3h at 25 ºC. The resulted nano boehmite was filtered and washed by distilled water and were kept in the oven at 220 ºC for 4 h. The obtained boehmite nanoparticles (1.5 g) was dispersed in 50 mL toluene by sonication for 30 min, and then 2.5 mL of (3-choloropropyl)triethoxysilane (CPTES) was added to mixture. The reaction mixture was stirred at 40 ºC for 8 h. Then, the prepared nanoparticles (nPr-Cl-boehmite) was filtered, washed with ethanol and dried at room temperature. The obtained Cl-boehmite (1g) were dispersed in 50 mL ethanol for 20 min, and then S-methylisothiourea hemisulfate salt (2.5 mmol) and potassium carbonate (2.5 mmol) were added to the reaction mixture and stirred for 18 h at 80 ºC. Then, the resulting nanoparticles (SMTU-boehmite) was filtered, washed with ethanol and dried at room temperature. The TGA was used to determine the percentage of chemisorbed organic functional groups onto the boehmite nanoparticles. The obtained SMTU-boehmite (0.5 g) was dispersed in 25 mL ethanol by sonication for 20 min, and then palladium acetate (0.25 g) was added to the reaction mixture. The reaction mixture was stirred at 80 ºC for 20 h. Then, the $NaBH_4$ (0.3 mmol) was added to the reaction mixture and stirred for 2 hours. The final product (Pd(0)-SMTU-boehmite) was filtered, washed by ethanol and dried at room temperature. The amount of palladium determined by EDS and ICP-OES analysis.

4.3 Result of catalyst characterization

IR (KBr) cm^{-1}: 3384, 3098, 2101, 1631, 1568, 1418, 1111, 739, 692, 624, 480; **ICP-OES (amount of Pd) mol g^{-1}:** 2.55 × 10-3; **BET (at 120 °C for 3h):** $a_{s,BET}$ = 82.90 m^2/g, V_p = 0.19 cm^3/g, r_p =1.21 nm; **XRD (2θ / degree) at**: 14.40, 28.41, 38.55, 39, 46, 46.45, 49.55, 51.94, 56.02, 59.35, 65.04, 65.56, 67, 68.09, and 72.38;

4.4 General procedure for the Suzuki reaction

A mixture of aryl halide (1 mmol), phenylboronic acid (1 mmol) or 3,4-difluoro phenylboronic acid (1 mmol), Na_2CO_3 (1.5 mmol), and Pd(0)-SMTU-boehmite (0.005 g, 0.8 mol%) were added to a reaction vessel. The resulting mixture was stirred in H_2O at room temperature and the progress of reaction was monitored by TLC. After completion of the reaction, catalyst was separated and washed with ethylacetate. The reaction mixture was extracted with H_2O and ethylacetate and organic layer 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.

4.5 General procedure for the Heck reaction

A mixture of aryl halide (1 mmol), alkene (1.2 mmol), Na_2CO_3 (1.5 mmol), and Pd(0)-SMTU-boehmite (0.016 g, 2.56 mol%) was stirred in PEG-400 at 120 ºC (progress of the reaction was monitored by TLC). After completion of the reaction, the mixture was cooled to room temperature and then catalyst was separated, 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), evaporated to obtain pure products in 85 to 99% yields.

4.6 Selected spectral data

4-Methyl-1,1'-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 7.66-7.64 (m, 2H), 7.58-7.56 (m, 2H), 7.52-7.47 (m, 2H), 7.41-7.37 (tt, J= 7.2, 1.2 Hz, 1H), 7.33-7.31 (d, J= 8 Hz, 2H), 2.47 (s, 3H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ= 141.2, 138.4, 137.1, 129.6, 128.8, 127.1, 127.0, 21.2 ppm.

[1,1'-Biphenyl]-4-carbonitrile: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 7.78-7.75 (m, 2H), 7.73-7.70 (m, 2H), 7.64-7.61 (m, 2H), 7.54-7.50 (m, 2H), 7.48-7.44 (m, 1H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ= 145.7, 139.2, 132.7, 129.2, 128.7, 127.8, 127.3, 119.0, 110.1 ppm.

4-Chloro-1,1'-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$): δ_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; ^{13}C NMR (400 MHz, $CDCl_3$) δ= 140.0, 139.7, 133.5, 129.0, 128.9, 128.5, 127.7, 127.1 ppm.

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; ^{13}C NMR (400 MHz, $CDCl_3$) δ= 167.1, 144.6, 134.5, 130.2, 128.9, 128.1, 118.3, 64.5, 30.9, 19.2, 13.8 ppm.

Butyl 3-(p-tolyl)acrylate: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 7.71-7.67 (d, J= 16 Hz, 1H), 7.47-7.45 (d, J= 8 Hz, 2H), 7.23-7.21 (d, J= 8 Hz, 2H), 6.45-6.41 (d, J= 16 Hz, 1H), 4.25-4.22 (t, J= 13.2 Hz, 2H), 2.41 (s, 3H), 1.76-1.69 (quint, J= 6.4 Hz, 2H), 1.50-1.44 (sixt, J= 7.6 Hz, 2H), 1.02-0.98 (t, J= 7.6 Hz, 3H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ= 167.3, 144.6, 140.6, 131.8, 129.6, 128.1, 117.2, 64.4, 30.8, 21.5, 19.2, 13.8 ppm.

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

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(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; ^{13}C NMR (400 MHz, $CDCl_3$) δ= 167.4, 161.3, 144.2, 129.7, 127.2, 115.8, 114.3, 64.3, 55.3, 30.8, 19.2, 13.8 ppm.

3-(p-Tolyl)acrylonitrile: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 7.42-7.37 (m, 3H), 7.29-7.23 (m, 2H), 5.88-5.84 (d, *J*= 16.4 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ= 150.5, 140.2, 130.2, 129.1, 128.5, 118.4, 95.1, 21.3 ppm.

3,4-Difluoro-1,1'-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 7.80-7.74 (m, 1H), 7.70-7.68 (m, 2H), 7.56-7.52 (m, 2H), 7.50-7.45 (m, 2H), 7.42-7.38 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ= 151.5, 151.3, 150.8, 150.7, 149.1, 148.9, 148.4, 148.3, 138.4, 138.3, 138.3, 138.2, 138.2, 129.5, 128.4, 127.2, 123.9, 123.9, 123.8, 124.8, 118.4, 118.3, 116.3, 116.1 ppm.

3,4-Difluoro-4'-nitro-1,1'-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 8.33-8.29 (m, 2H), 8.02-7.99 (m, 2H), 7.97-7.94 (m,1H), 7.71-7.68 (m,1H), 7.65-7.58 (m, 1H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ= 151.8, 151.7, 151.6, 151.5, 149.3, 149.2, 149.2, 149.0, 147.4, 144.7, 135.9, 135.8, 135.8, 135.8, 128.5, 124.9, 124.9, 124.8, 124.8, 124.5, 118.8, 118.7, 117.2, 117.0 ppm.

Acknowledgements

This work was supported by the research facilities of Ilam University, Ilam, Iran.

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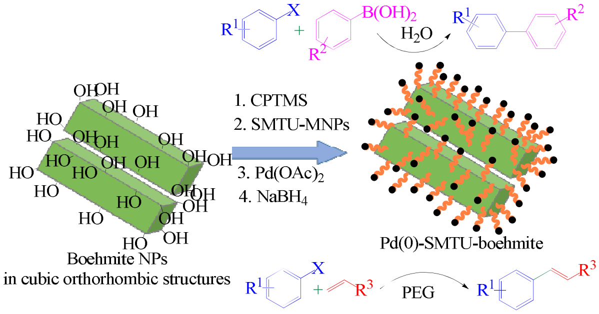
DOI: 10.1039/C6RA02967A

Graphical Abstract

Synthesis of new Pd(0)-complex supported on boehmite nanoparticles and study of its catalytic activity for Suzuki and Heck reactions in H2O or PEG

Arash Ghorbani-Choghamarani,* Parisa Moradi, Bahman Tahmasbi



Pd(0)-SMTU-boehmite was prepared using commercially materials and was applied as moisture-and air-stable nanocatalyst in C-C coupling in H_2O or PEG-400.