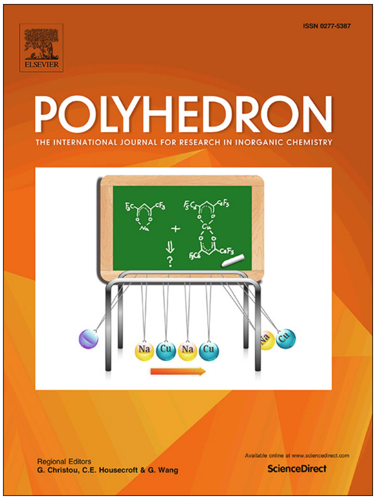

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Modification of boehmite nanoparticles with Adenine for the immobilization of Cu(II) as organic-inorganic hybrid nanocatalyst in organic reactions

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ABSTRACT

Boehmite nanoparticles are aluminum oxide hydroxide (γ-AlOOH) particles, which has large specific surface area (>120 m^2g^{-1}) and can be prepared using an inexpensive procedure in water. Herein, we present an economical, simple, and environmentally friendly route for the preparation of a copper catalyst on Adenine coated boehmite nanoparticles (Cu-Adenine@boehmite). This catalyst has been characterized by several techniques such as SEM, XRD, AAS, ICP and TGA analysis. Cu-Adenine@boehmite was applied as highly efficient and reusable nanocatalyst in carbon-carbon coupling reactions between various aryl halides and sodium tetraphenyl borate, phenylboronic acid, or 3,4-diflorophenylboronic acid under aerobic conditions, palladium-free and phosphine-free ligand. Also this catalyst was applied for the synthesis of polyhydroquinoline derivatives. In continuation, selective oxidation of sulfides to sulfoxides using hydrogen peroxide (H_2O_2) was studied in the presence of Cu-Adenine@boehmite as catalyst. The synthesis of sulfoxides using H_2O_2 in the presence of Cu-Adenine@boehmite does not generate waste and any byproducts. This catalyst was reused for several times in C-C coupling reaction without loss of its catalytic activity. Reused catalyst was characterized by SEM, XRD and ICP techniques.

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Heterogeneity and stability of Cu-Adenine@boehmite were studied by hot filtration test, poisoning test and ICP analysis.

Keywords: Boehmite nanoparticles, Copper, Suzuki reaction, Polyhydroquinoline, Sulfoxide.

1. Introduction

Recently the nanomaterials widely attracted much attention, because they are as a precursor of inorganic-organic hybrid materials [1-6]. Also they have excellent applications in catalytic reactions, adsorption materials, optical and environmental problems, food processing, medical industry, energy production and they have used in various fields of chemistry, physics, engineering and science [7-10]. Boehmite (γ-AlOOH) is one of the polymorph phase of aluminum oxihydroxide and inorganic lamellar compound. Boehmite is aluminum oxide hydroxide that was formed by octahedral units of six oxygen atoms around the central aluminum [10, 11]. Because, boehmite has only two elements (aluminum and oxygen), it can be used as a high environmentally friendly and inexpensive material in different processes. Therefore, several methods have been reported for the synthesis of boehmite nanoparticles such as hydrothermal [12, 13], coprecipitation [14, 15], sol-gel [16] and hydrolysis of aluminum [17]. Among various preparation procedures of boehmite nanoparticles, the hydrothermal method has several advantages such as production in a one-pot process, green conditions and needs a low temperature for preparation of nanoparticles [7, 18, 19]. The well-crystallized boehmite is easily fabricated by a hydrothermal treatment using suspension of an aluminum salt (such as $Al(NO_3)_3.9H_2O$ and aluminum chloride hexahydrate) or aluminum trihydroxide (such as bayerite and gibbsite) in water [19-22]. Moreover, the morphology and size of boehmite nanoparticles can be controlled in hydrothermal method, which make boehmite as useful material for various applications in industrial point of view [21-24]. Thermal stability, non-toxicity, ease of surface modification, mesoporous properties, high specific surface area (>120 m^2g^{-1}) of boehmite nanoparticles are major advantages for its catalytic application [25-27]. Meanwhile, boehmite nanoparticles have been rarely applied as support for the preparation of heterogeneous catalysts [28-31]. Therefore herein we have reported a new procedure for the preparation of supported copper (II) on Adenine coated boehmite nanoparticles (Cu-Adenine@boehmite), which successfully applied as highly efficient and recoverable catalyst for the carbon-carbon cross coupling reactions, synthesis of polyhydroquinoline derivatives and selective oxidation of sulfides to sulfoxides.

Carbon-carbon coupling reactions are powerful tools for the preparation of advanced materials, natural products, pharmaceuticals, agrochemicals, herbicides, biologically active compounds, UV screens, polymers, hydrocarbons and liquid crystal materials [32-35]. Suzuki reaction is usually reported with homogeneous or heterogeneous palladium catalysts [36-39]. The use of palladium phosphine-based catalyst led to expensive, toxic, air and moisture sensitive procedure. Also, use of phosphine ligands suffer from several drawbacks such as thermal instability and non-recoverability [40, 41]. Therefore, use of copper catalyst is environmentally friendly and inexpensive rather than palladium catalysts. Additionally, copper catalyst is not moisture- or air-sensitive, and have been synthesized and used without an inert atmosphere or phosphine ligands. Therefore, with respect to green chemistry principles, we have reported immobilized Cu(II) on modified boehmite nanoparticles as stable and reusable catalyst for the Suzuki C-C coupling reaction.

The selective oxidation of sulfides to corresponding sulfoxides is an important transformation in organic functional groups, because sulfoxides play an important role in organic synthesis, enzymes activation, separation of radioactive or less common metals [42-44], and in medicinal chemistry as antihypertensive, antibacterial, antifungal, anti-ulcer, anti-atherosclerotic agents, cardiotonic agents and so on [42, 45, 46]. However, transformation of sulfides to sulfoxides have been reported using both organic and inorganic reagents, which lead to toxic wastes byproducts [47-49]. Therefore, to keep pace green chemistry principles, herein we have used hydrogen peroxide as oxidant in the oxidation of sulfides in the presence of Cu-Adenine@boehmite as catalyst. Because, use of H_2O_2 as oxidant for the transformation of sulfides to sulfoxides offers several advantages such as cheapness, readily available, and environmentally friendly oxidant with the water as only byproduct [50]. Also, multicomponent reactions has emerged as a powerful tool for the synthesis of biological and organic compounds, which have several advantages such as one-pot synthetic pathway, high atom economy and time saving without isolation of any intermediates or generating any by-products [51-54]. Among different heterocyclic compounds, polyhydroquinoline derivatives have a wide range of biological activities such as antitumor, bronchodilator, vasodilator, antiatherosclerotic and antidiabetic properties [50-58]. For example, polyhydroquinoline derivatives are a significant class of well-known Ca^{2+} channel blockers and establish the skeletons of drug molecules utilized for the treatment of hypertension and cardiovascular diseases [58, 59]. Therefore, the synthesis of polyhydroquinoline derivatives is an area of remarkable attention in organic chemistry.

2. Experimental:

2.1. Preparation of catalyst

In the first step, boehmite nanoparticles were prepared and further modified by (3-chloropropyl)-trimethoxysilane (CPTMS@boehmite) according to the new reported procedure [20]. In order to modify boehmite nanoparticles with adenine, 1 g of CPTMS@boehmite was dispersed in toluene and mixed with 2 mmol of adenine. Then, this mixture was stirred at 90 °C for 48 h. The resulting solid (Adenine@boehmite) was separated using simple filtration, washed with ethanol and dried at room temperature. In the final step, 1.0 g of Adenine@boehmite and 2 mmol of $Cu(NO_3)_2.9H_2O$ were dispersed in ethanol and stirred for 20 hours under reflux conditions. The solid product (Cu-Adenine@boehmite) was obtained by filtration, washed with ethanol and water and dried at 50 °C.

2.2. General procedure for C-C coupling reaction through Suzuki reaction

1 mmol of aryl halide, 0.5 mmol of sodium tetraphenyl borate or 1 mmol of phenylboronic acid or 1 mmol of 3,4-diflorophenylboronic acid, 1.5 mmol of sodium carbonate, and 20 mg of Cu-Adenine@boehmite (containing 0.40 mol % of Cu) were stirred in water at 80 ºC and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled down to room temperature and catalyst was separated by simple filtration and washed with ethyl acetate and 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.

2.3. General procedure for the synthesis of polyhydroquinoline derivatives

A mixture of aldehyde (1 mmol), dimedon (1 mmol), ethylacetoacetate (1 mmol), ammonium acetate (1.3 mmol) and Cu-Adenine@boehmite (20 mg, 0.40 mol% of Cu) were stirred in ethanol under reflux conditions and the progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by simple filtration and washed with ethanol. Then, the solvent was evaporated and all products was recrystallized in ethanol.

2.4. General procedure for the oxidation of sulfides to sulfoxides

0.008 g (0.17 mol %) of Cu-Adenine@boehmite was added to a solution of sulfide (1 mmol) and 0.4 mL of H_2O_2 (33%), the mixture was stirred under solvent free conditions at room temperature for the specified time (Table 6) and the progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by simple filtration. The product was extracted with water and ethyl acetate and dried over anhydrous Na_2SO_4 (1.5 g). Then, the solvent was evaporated and pure products were obtained in high yields.

2.5. Selected spectral data

[1,1'-Biphenyl]-4-carbonitrile: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 7.77-7.75 (d, *J*= 8 Hz, 2H), 7.73-7.71 (d, *J*= 8 Hz, 2H), 7.64-7.63 (d, *J*= 4 Hz, 2H), 7.55-7.51 (t, *J*= 8 Hz, 2H), 7.49-7.46 (t, *J*= 8Hz, 1H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ = 145.6, 139.2, 132.6, 129.1, 128.7, 127.8, 127.3, 119.0, 110.9 ppm.

4-Nitro-1,1'-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 8.36-8.32 (d, *J*= 8 Hz, 2H), 7.79-7.76 (d, *J*= 8 Hz, 2H), 7.68-7.66 (d, *J*= 8 Hz, 2H), 7.56-7.52 (t, *J*= 8 Hz, 2H), 7.51-7.47 (t, *J*= 8Hz, 1H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ = 147.6, 147.1, 138.8, 129.2, 128.9, 127.8, 127.4, 124.1 ppm.

3,4-Difluoro-4'-nitro-1,1'-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 8.35-8.33 (d, *J*= 8 Hz, 2H), 7.73-7.71 (d, *J*= 8 Hz, 2H), 7.50-7.45 (m, 1H), 7.42-7.38 (m, 1H), 7.36-7.30 (m, 1H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ = 152.2, 149.5, 147.4, 145.3, 135.8, 127.4, 124.3, 123.6, 118.2, 116.5 ppm.

Ethyl 4-(3,4-dimethoxyphenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 6.96 (s, 1H), 6.83-6.81 (d, *J*= 8Hz, 1H), 6.74-6.72 (d, *J*= 8Hz, 1H), 6.12 (s, 1H), 5.04 (s, 1H), 4.13-4.08 (q, *J*= 8 Hz, 2H), 3.86 (s, 3H), 3.83 (s, 3H), 2.41 (s, 3H), 2.38-2.29 (t, *J*= 16 Hz, 2H), 2.25-2.18 (dd, *J*= 16, 8 Hz, 2H), 1.27-1.23 (t, *J*= 8 Hz, 3H), 1.10 (s, 3H), 0.98 (s, 3H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ = 195.6, 167.5, 148.2, 147.9, 147.2, 143.2, 140.0, 119.8, 112.3, 111.9, 110.7, 106.2, 59.8, 55.8, 55.7, 50.8, 41.1, 35.9, 32.7, 29.5, 27.1, 19.5, 14.3 ppm.

Ethyl 4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate: ^{1}H NMR (400 MHz, CDCl$_3$): δ_H= 7.28-7.26 (d, *J*= 8Hz, 2H), 7.20-7.18 (d, *J*= 8Hz, 2H), 7.03 (br, 1H), 5.05 (s, 1H), 4.12-4.07 (q, *J*= 8 Hz, 2H), 2.37 (s, 3H), 2.31-2.14 (m, 4H), 1.25-1.21 (t, *J*= 8 Hz, 3H), 1.08 (s, 3H), 0.94 (s, 3H) ppm; ^{13}C NMR (400 MHz, CDCl$_3$, ppm) δ = 195.8, 167.3, 149.3, 145.7, 144.1, 131.6, 129.4, 128.0, 111.5, 105.6, 59.9, 50.8, 40.8, 36.3, 32.7, 29.5, 27.1, 19.3, 14.3 ppm.

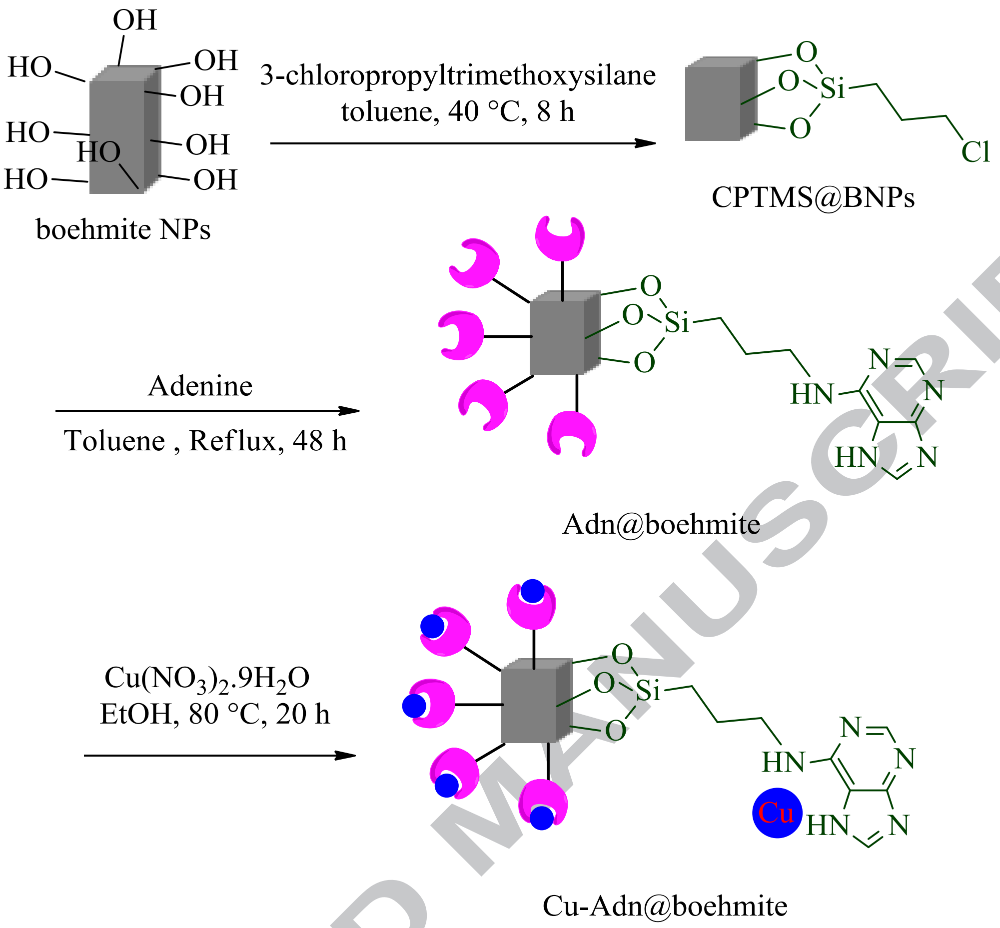
Ethyl4-(4-fluorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate: ^{1}H NMR (400 MHz, CDCl$_3$): δ_H= 7.31-7.27 (t, *J*= 8Hz, 2H), 6.92-6.88 (t, *J*= 8Hz, 2H), 6.27 (br, 1H), 5.06 (s, 1H), 4.11-4.06 (q, *J*= 8 Hz, 2H), 3.39 (s, 3H), 3.37-2.28 (t, *J*= 16 Hz, 2H), 2.24-2.15 (m, 2H), 1.24-1.20 (t, *J*= 8 Hz, 3H), 1.10 (s, 3H), 0.95 (s, 3H) ppm; ^{13}C NMR (400 MHz, CDCl$_3$, ppm) δ = 195.6, 167.3, 162.5, 160.0, 148.2, 143.5, 142.9, 129.4, 114.7, 114.5, 112.1, 106.2, 59.9, 50.8, 41.0, 36.0, 32.7, 29.4, 27.1, 19.4, 14.2 ppm.

2-(Phenylsulfinyl)ethanol: ^{1}H NMR (400 MHz, CDCl$_3$): δ_H= 7.89-7.87 (d, *J*= 8 Hz, 1H), 7.61-7.60 (d, *J*= 4 Hz, 2H), 7.48-7.47 (d, *J*= 4 Hz, 2H), 4.20 (br, 1H), 4.13-3.86 (m, 2H), 3.08-2.90 (m, 2H) ppm; ^{13}C NMR (400 MHz, CDCl$_3$, ppm) δ = 142.9, 131.2, 129.4, 123.9, 59.9, 55.9 ppm.

(Methylsulfinyl)benzene: ^{1}H NMR (400 MHz, CDCl$_3$): δ_H= 7.92-7.89 (d, *J*= 12 Hz, 1H), 7.62-7.60 (m, 2H), 7.49-7.47 (m, 2H), 2.69 (s, 3H) ppm; ^{13}C NMR (400 MHz, CDCl$_3$, ppm) δ = 145.5, 131.1, 129.4, 123.5, 43.9 ppm.

3. Result and discussion

Initially, Cu-Adenine@boehmite was prepared based on Scheme 1 and characterized by thermogravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD), atomic absorption spectroscopy (AAS), and inductively coupled plasma (ICP-OES) techniques.



Scheme 1. Synthesis of Cu-Adenine@boehmite.

3.1. Catalyst characterizations

The particles size and morphology of Cu-Adenine@boehmite were studied by scanning electron microscopies (SEM) technique. SEM image of this catalyst is shown in Figure 1. As shown, the particles of catalyst were obtained with size of 60-90 nm of diameters. Also, the exact amount of copper that is loaded on boehmite nanoparticles was found to be 0.20×10^{-3} mol g^{-1} based on results of inductively coupled plasma (ICP). This result is good agreement with atomic absorption spectroscopy (AAS) that is indicate 0.22×10^{-3} mol g^{-1} of copper in catalyst.

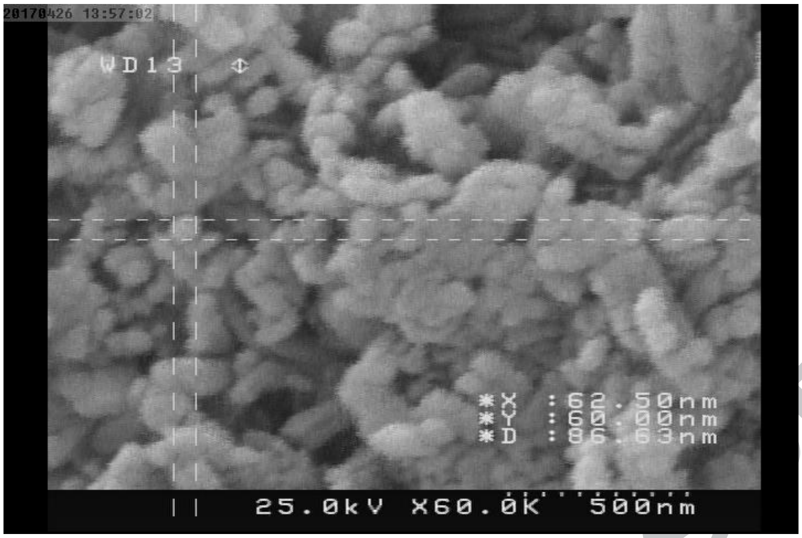


Figure 1. SEM image of Cu-Adenine@boehmite.

The XRD pattern of Cu-Adenine@boehmite is shown in Figure 2. As shown in Figure 2, the peak positions of 2θ at 13.58, 28.49, 38.51, 45.89, 49.35, 51.51, 56.49, 60.65, 64.07, 65.19, 68.27, and 72.57 are in agreement with standard XRD pattern of boehmite nanoparticles and all peaks strongly confirmed the crystallization of boehmite nanoparticles in orthorhombic unit cells [3, 11].

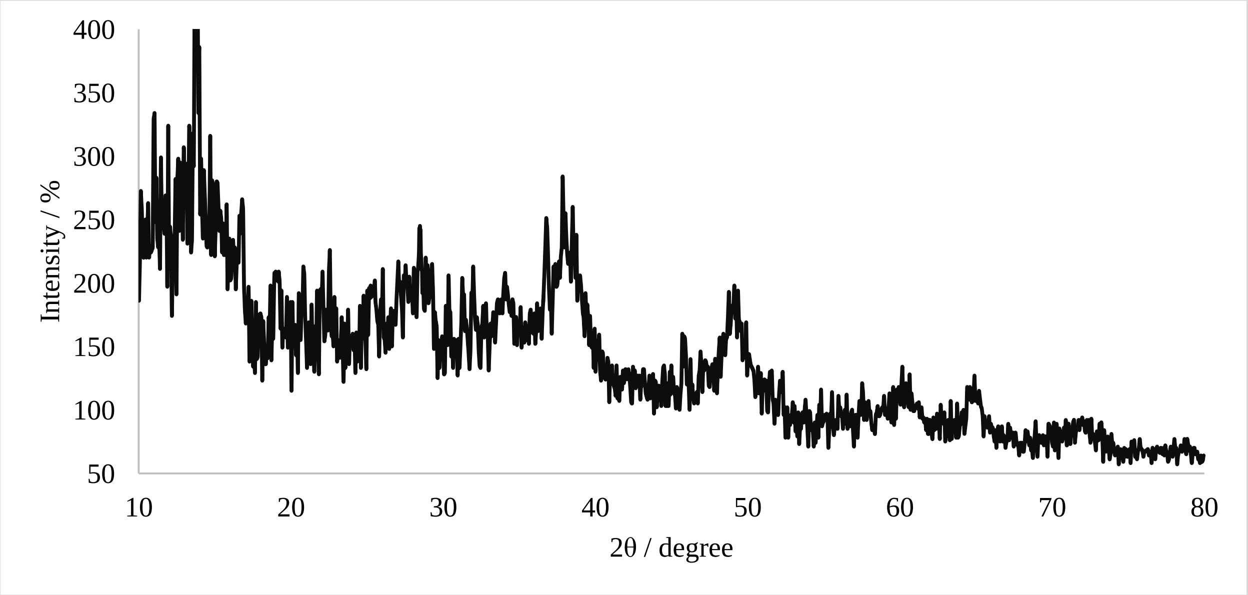


Figure 2. XRD pattern of Cu-Adenine@boehmite.

TGA/DTA diagrams of Cu-Adenine@boehmite are shown in Figure 3. The TGA curve of catalyst shows the several steps of weight loss. The small mass loss in low temperatures (below 100 °C) about 7% is corresponded to the removal of adsorbed water, solvents and surface hydroxyl groups [24-27]. Second weight loss (35 %) between 250-600 °C is related to calcination of organic layers that are immobilized on boehmite nanoparticles. Final weight loss (about 3%) in high temperatures that is happened above 600 °C, may be related to thermal transformation of crystal phase of boehmite nanoparticles [34, 42]. On the basis of these results, the well supporting of Adenine on the surface of boehmite nanoparticles was confirmed.

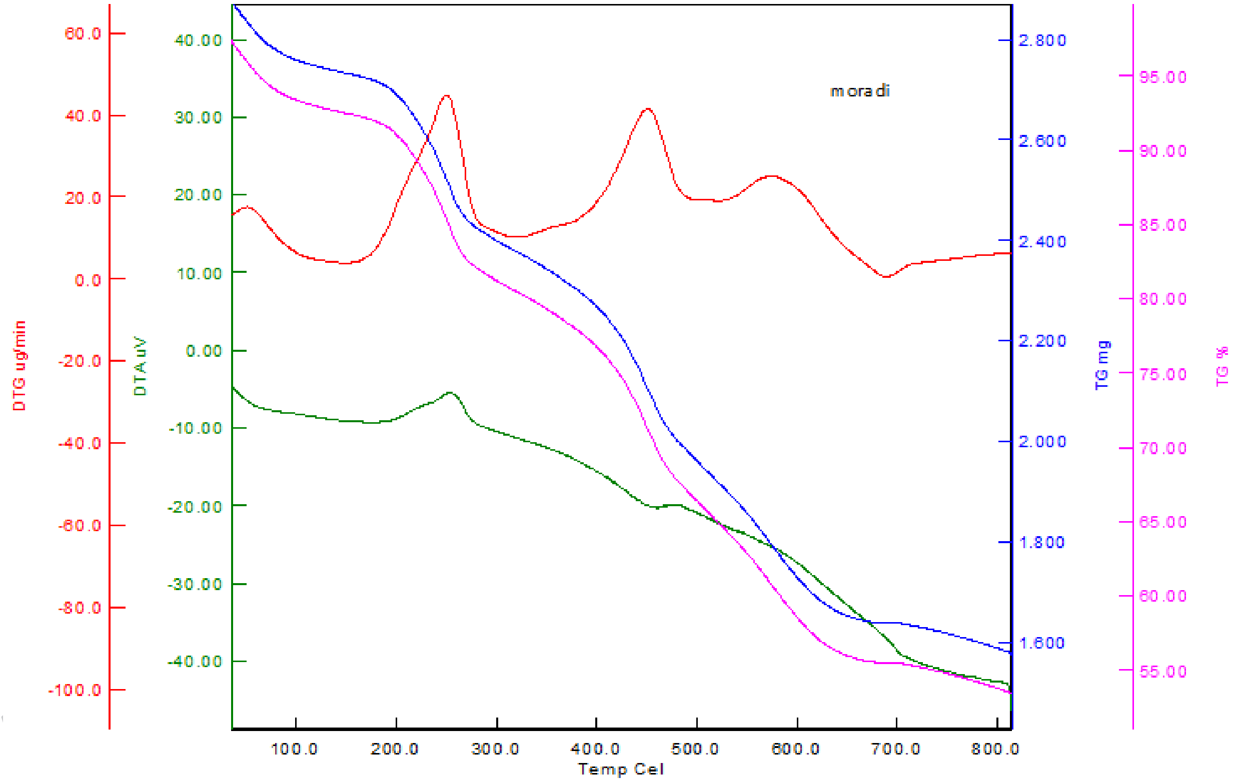
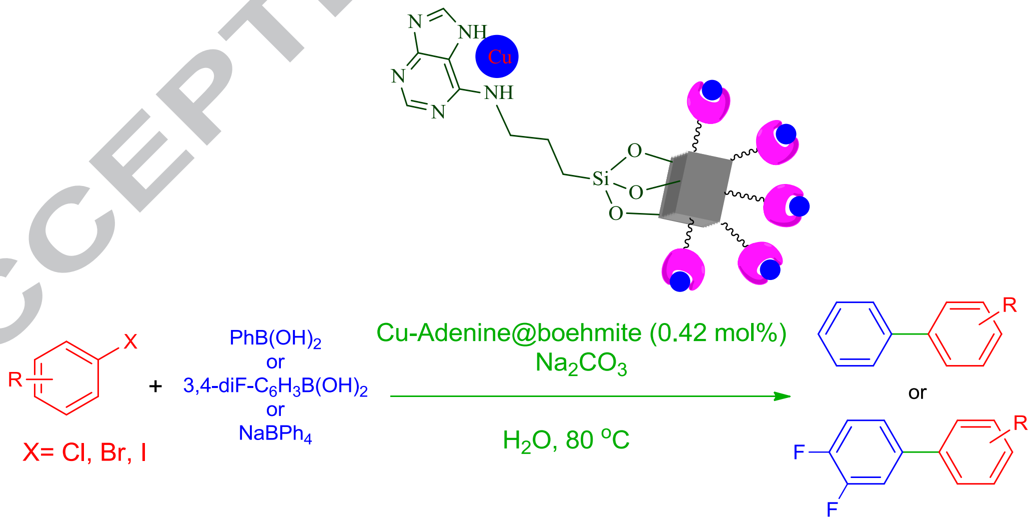


Figure 3. TGA/DTA diagrams of Cu-Adenine@boehmite.

3.2. Application of Cu-Adenine@boehmite in Suzuki reaction

Catalytic activity of Cu-Adenine@boehmite was studied in various organic reactions such as C-C coupling reaction, synthesis of polyhydroquinoline derivatives and selective oxidation of sulfides to sulfoxides. At first, C-C coupling reaction in the presence of Cu-Adenine@boehmite has been studied (Scheme 2). In order to optimize the amount of catalyst in Suzuki reaction, the reaction of iodobenzene with phenylboronic acid was investigated in the presence of different amount of Cu-Adenine@boehmite. The best amount of catalyst was found to be 20 mg of Cu-Adenine@boehmite (containing 0.40 mol% of Cu). In the next step, the C-C coupling reaction of iodobenzene and phenylboronic acid in different solvents carried out in the presence of Cu-Adenine@boehmite (20 mg). Based on the obtained results (Table 1), water showed a better conversion in model reaction. Temperature and nature of base have been also studied and the best results were obtained using 1.5 mmol of Na_2CO_3 at 80 °C. These results are summarized in Table 1.



Scheme 2. Carbon-Carbon coupling reaction of aryl halides with phenylboronic acid, sodium tetraphenyl borate or 3,4-diF-$C_6H_3B(OH)_2$ in the presence of Cu-Adenine@boehmite

Table 1. Optimization of Suzuki reaction conditions for coupling of iodobenzene with phenylboronic acid in the presence of Cu-Adenine@boehmite.

Entry	Catalyst (mg)	Solvent	Base	Temperature (ºC)	Time (min)	Yield (%)[a]
1	15	PEG	Na_2CO_3	80	120	50
2	20	PEG	Na_2CO_3	80	120	62
3	25	PEG	Na_2CO_3	80	120	64
4	20	DMF	Na_2CO_3	80	100	90
5	20	EtOH	Na_2CO_3	reflux	120	24
6	20	Dioxane	Na_2CO_3	80	120	27
7	**20**	**H_2O**	**Na_2CO_3**	**80**	**60**	**98**
8	20	DMSO	Na_2CO_3	80	70	95
9	20	H_2O	NaOH	80	120	69
10	20	H_2O	Et_3N	80	120	40
11	20	H_2O	NaOEt	80	120	Trace
12	20	H_2O	Na_2CO_3	50	120	Trace
13	20	H_2O	Na_2CO_3	r.t.	120	-[b]

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

Under the optimized reaction conditions, the scope of this procedure was explored with various aryl halides and phenylboronic acid derivatives (Table 2). As shown in Table 2, the coupling of phenylboronic acid with phenyl iodides performed in shorter reaction times than phenyl bromides or phenyl chlorides. Aryl halides bearing an electron-donating (Table 2, entries 8-12) or electron-withdrawing (Table 2, entries 4-7) groups were converted to the corresponding biphenyles in high yields.

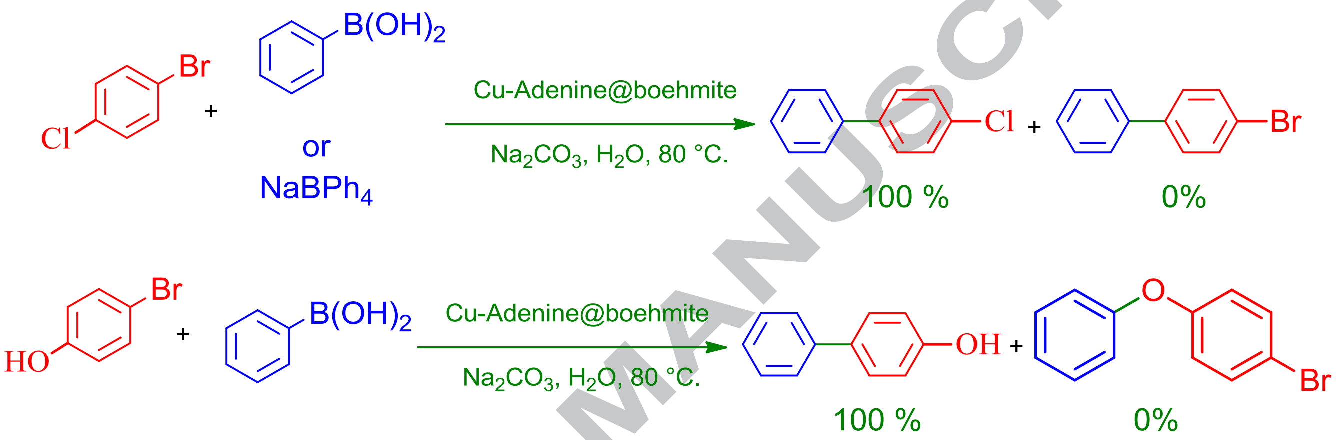
In order to extend the scope of our methodology, we next investigated the coupling of various aryl halides with sodium tetraphenyl borate (Table 2, entries 11-14) and 3,4-diF-$C_6H_3B(OH)_2$ (Table 2, entries 15, 16). As expected, aryl iodides were more reactive than aryl bromides. As shown in Table 2, high catalytic activity of Cu-Adenine@boehmite was observed in C-C coupling reaction (Suzuki reaction). All products were obtained in high TON and TOF values. In order to show the selectivity of this catalytic system, 1-bromo-4-chorobenzene considered in coupling reaction with phenylboronic acid and sodium tetraphenyl borate (Table 2, entries 5, 13). As shown in Scheme 3, chloro functional group remained intact during the Suzuki reaction, and coupling of bromo functional group was observed as only product. Also as shown in Table 2 (Entry 6), coupling of C-O was not observed and pure biphenyl was obtained in 93% of yield. Therefore, this experimental procedure is capable for coupling of various aryl halides including Cl, Br and I in the presence of Cu-Adenine@boehmite as catalyst. The experimental procedure is very simple, effective, and has ability to tolerate a variety of different electron-donor and electron-withdrawing functional groups.

Table 2. Catalytic C-C coupling reaction of aryl halides with phenylboronic acid, sodium tetraphenyl borate and 3,4-diF-$C_6H_3B(OH)_2$ in the presence of Cu-Adenine@boehmite (0.40 mol%) in H_2O at 80 °C.

Entry	Aryl halide	phenylating reagent	Time (min)	Yield (%)^a	TON	TOF (h^{-1})	Melting point (°C)	Reported M.P. [Ref.]
1	Iodobenzene	$PhB(OH)_2$	60	98	245	245	65-67	64-66 [34]
2	Bromobenzene	$PhB(OH)_2$	150	87	217	87	64-67	64-66 [34]
3	Chlorobenzene	$PhB(OH)_2$	190	92	230	73	64-67	64-66 [34]
4	4-Bromonitrobenzene	$PhB(OH)_2$	45	93	232	310	110-112	110-113 [24]
5	4-Bromochlorobenzene	$PhB(OH)_2$	270	90	225	50	69-72	69-71 [24]
6	4-Chloronitrobenzene	$PhB(OH)_2$	90	86	215	143	111-114	110-113 [24]
7	4-Bromobenzonitrile	$PhB(OH)_2$	75	87	217	174	84-87	86-88 [24]
8	4-Bromophenol	$PhB(OH)_2$	200	93	232	70	158-161	157-160 [24]
9	4-Bromotoluene	$PhB(OH)_2$	100	96	240	144	42-44	42-44 [34]
10	4-Iodotoluene	$PhB(OH)_2$	90	95	237	158	41-43	42-44 [34]
11	4-Iodotoluene	$NaBPh_4$	90	89	222	148	42-43	42-44 [34]

12	Iodobenzene	$NaBPh_4$	65	94	235	217	67-68	64-66 [34]
13	4-Bromochlorobenzene	$NaBPh_4$	250	93	232	56	69-71	69-71 [24]
14	4-Bromonitrobenzene	$NaBPh_4$	50	94	235	282	110-111	110-113 [24]
15	Iodobenzene	3,4-diF-$C_6H_3B(OH)_2$	75	91	227	182	39-42	39-41 [24]
16	4-Bromonitrobenzene	3,4-diF-$C_6H_3B(OH)_2$	100	90	225	135	119-122	119-120 [24]

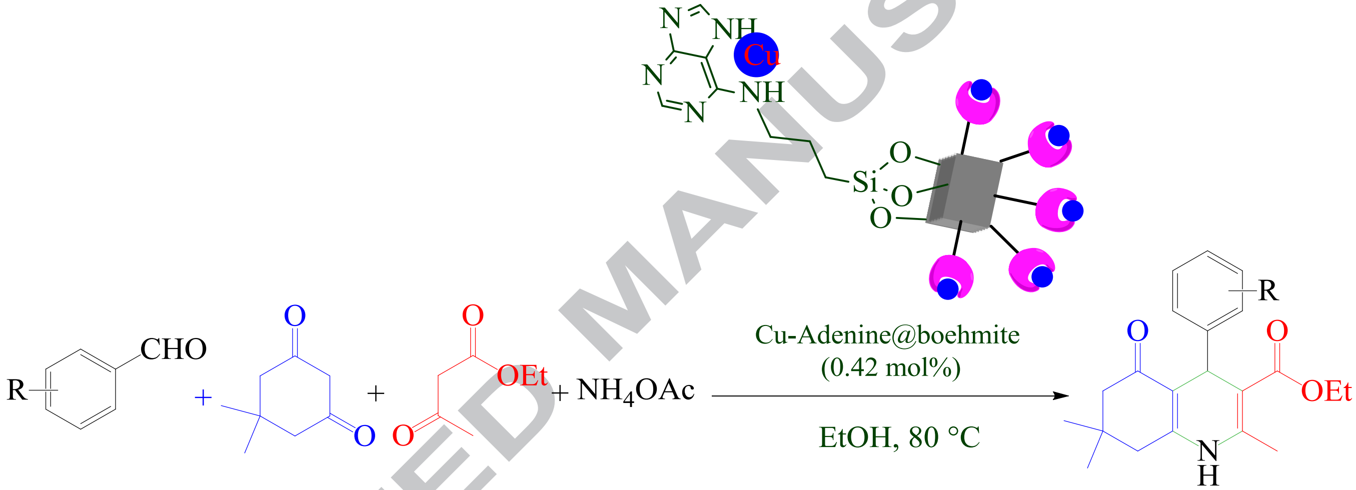
[a] Isolated yield.



Scheme 3. Selectivity in C-C coupling in the presence of Cu-Adenine@boehmite.

3.3. Application of Cu-Adenine@boehmite in the synthesis of polyhydroquinolines

Also, catalytic activity of Cu-Adenine@boehmite has been studied for the synthesis of polyhydroquinoline derivatives (Scheme 4). The condensation of benzaldehyde with dimedon, ethyl acetoacetate, and ammonium acetate was selected as model reaction to found the best conditions. Effect of various parameters on this reaction were studied and the results are summarized in Table 3. The model reaction has been examined in the presence of different amount of Cu-Adenine@boehmite. As shown in Table 3, low yield of product was obtained in the absent of catalyst even long reaction time. The results in Tablte 3 indicate that 20 mg (0.40 mol%) of Cu-Adenine@boehmite is required for the synthesis of desired product. The less amount of Cu-Adenine@boehmite gave a low yield, and the more amount of Cu-Adenine@boehmite could not cause to increase the yield of the corresponding product. Also, model reaction was studied in various solvents such as water, ethanol, ethyl acetate, acetonitrile and PEG-400. As it can be seen, maximum yield (97%) of product was achieved in ethanol as solvent. Finally, the effect of temperature was studied in model reaction (Table 3, entries 7-9). The reaction not proceeded at room temperature even in long reaction time. But, the best results were obtained at 80°C. Therefore, the reaction was kept at 80 °C.



Scheme 4. Synthesis of polyhydroquinoline derivatives in the presence of Cu-Adenine@boehmite.

Table 3. Optimization conditions for the synthesis of polyhydroquinolines *via* condensation of benzaldehyde with dimedon, ethyl acetoacetate, and ammonium acetate in the presence of Cu-Adenine@boehmite.

Entry	**Catalyst (mg)**	**Solvent**	**Temperature (ºC)**	**Time (min)**	**Yield (%)**[a]
1	15	EtOH	Reflux	75	69
2	20	EtOH	Reflux	75	97
3	25	EtOH	Reflux	70	98
4	20	H_2O	80	100	33
5	20	PEG	80	75	71

6	20	Ethyl acetate	Reflux	100	52
7	20	CH_3CN	Reflux	100	64
8	20	EtOH	60	80	70
9	20	EtOH	40	80	48

[a] Isolated yield

This optimized reaction conditions have been applied for the synthesis of various polyhydroquinoline derivatives in the presence of Cu-Adenine@boehmite (Table 4). A wide range of benzaldehydes including electron-donating and electron-withdrawing functional groups were successfully converted to polyhydroquinoline derivatives, and all products were obtained in good to excellent yields. Melting points of all products were found to be in good agreement with reported melting point in the authentic literatures. High efficiency of Cu-Adenine@boehmite in synthesis of polyhydroquinolines was confirmed by high TON and TOF values.

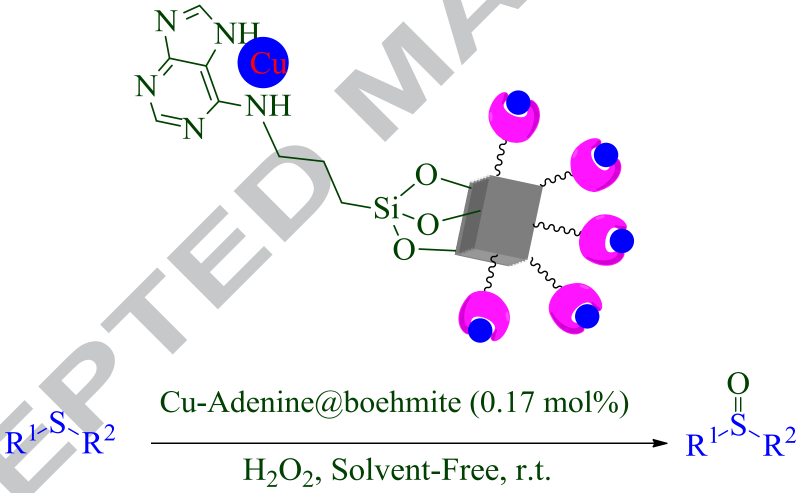
Table 4 Synthesis of polyhydroquinoline derivatives in the presence of Cu-Adenine@boehmite in ethanol under reflux conditions.

Entry	**Aldehyde**	**Time (min)**	**Yield (%)[a]**	**TON**	**TOF (h^{-1})**	**Melting point (^{o}C)**	**Reported M.P. [Ref.]**
1	4-Hydroxybenzaldehyde	20	91	227	682	227-230	228-230 [55]
2	3,4-Dimethoxybenzaldehyde	25	94	235	564	201-204	200-202 [60]
3	4-Chlorobenzaldehyde	120	95	237	119	234-236	233-235 [58]
4	4-Methoxybenzaldehyde	105	97	242	138	254-256	258-260 [55]
5	Benzaldehyde	75	97	242	194	202-205	203-204 [56]
6	3-Hydroxybenzaldehyde	50	89	222	267	226-228	228-230 [60]
7	3-Nitrobenzaldehyde	120	90	225	112	176-178	175-176 [56]
8	4-Fluorobenzaldehyde	100	91	227	136	183-185	185-187 [55]
9	4-Bromobenzaldehyde	100	94	235	141	252-254	253-255 [55]
10	4-Ethoxybenzaldehyde	60	91	227	227	173-174	176-178 [60]

[a]Isolated yield.

3.4. Application of Cu-Adenine@boehmite for the oxidation of sulfides

Also, catalytic activity of Cu-Adenine@boehmite was studied in the selective oxidation of sulfides to sulfoxides (Scheme 5). Oxidation of methyl phenyl sulfide was selected as model reaction to optimize the reaction conditions. In order to obtain suitable solvent and amount of catalyst, model reaction was examined in the presence of different amount of Cu-Adenine@boehmite and in different solvents (Table 5). As shown in Table 5, the best results were obtained in the presence of 8 mg (0.17 mol%) of Cu-Adenine@boehmite when the reaction was performed under solvent-free conditions at room temprature (Table 5, entry 2).



Scheme 5. Oxidation of sulfides to sulfoxides in the presence of Cu-Adenine@boehmite.

Table 5. Optimization of reaction conditions for the oxidation of methyl phenyl sulfide in the presence of Cu-Adenine@boehmite at room temperature.

Entry	Catalyst (mg)	Solvent	Time (min)	Yield (%)[a]
1	6	solvent free	80	62
2	8	solvent free	60	98
3	10	solvent free	55	99

4	8	CH_2Cl_2	60	85
5	8	CH_3CN	60	60
6	8	Ethyl acetate	60	55
7	8	Ethanol	60	33
8	8	H_2O	60	44

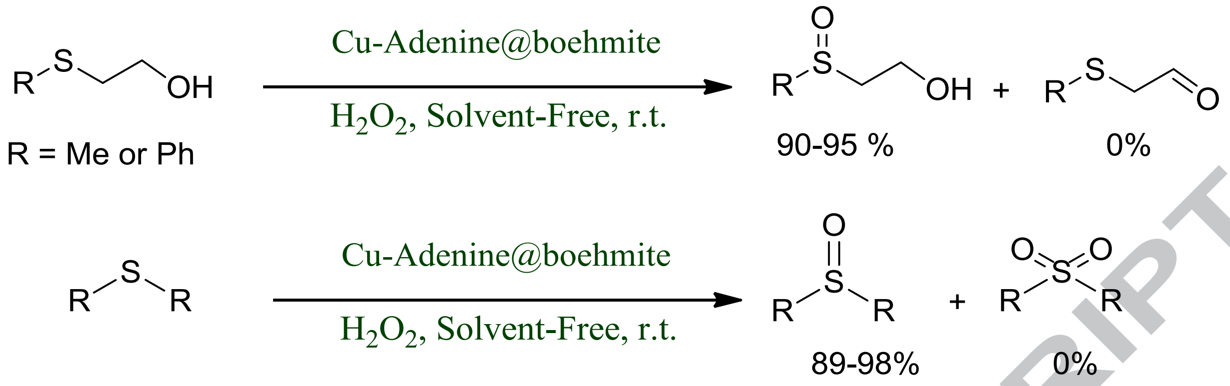
[a] Isolated yield.

We have generalized the applicability of this method for the selective oxidation of a variety of sulfides for the synthesis of sulfoxides (Table 6). Various aromatic, aliphatic and heterocyclic sulfides were successfully evaluated and sulfoxides were obtained in good to excellent yields and high TON and TOF values. Synthesis of sulfone as byproduct due to over oxidation was not observed (Scheme 6). It was found that the aromatic sulfides reacted in longer times in comparison with aliphatic ones. Also, other functional groups such as hydroxyl groups remained intact during the oxidation of sulfides to sulfoxides (Scheme 6).

Table 6. Selective oxidation of sulfides to sulfoxides for the presence of Cu-Adenine@boehmite.

Entry	**Sulfide**	**Time (min)**	**Yield (%)[a]**	**TON**	**TOF (h^{-1})**	**Melting point (ºC)**	**Reported M.P. [Ref.]**
1	Methyl phenyl sulfide	60	98	576	576	29-32	30-32 [42]
2	2-Phenylthioethanol	10	95	559	3352	Oil	Oil [20]
3	Dipropylsulfane	10	96	567	3388	Oil	Oil [61]
4	Tetrahydrothiophene	5	98	576	6917	Oil	Oil [62]
5	2-Methylthioethanol	20	90	529	1588	Oil	Oil [20]
6	Methyl(undecyl)sulfane	80	89	523	392	60-63	61-64 [42]
7	Dibutylsulfane	20	95	559	1676	Oil	Oil [20]

[a] Isolated yield.



Scheme 6. Selective oxidation of sulfides to sulfoxides in the presence of Cu-Adenine@boehmite as catalyst.

3.5. Reusability Study

The recyclability of the catalysts is a great and important factor in catalytic studies. Therefore, reusability of Cu-Adenine@boehmite as catalyst was considered in the coupling of iodobenzene with phenylboronic acid under optimized reaction conditions (Figure 4). In the end of the reaction, catalyst was isolated by centrifugation, washed with ethyl acetate and residual catalyst was reused up to 8 times without lose of catalytic activity.

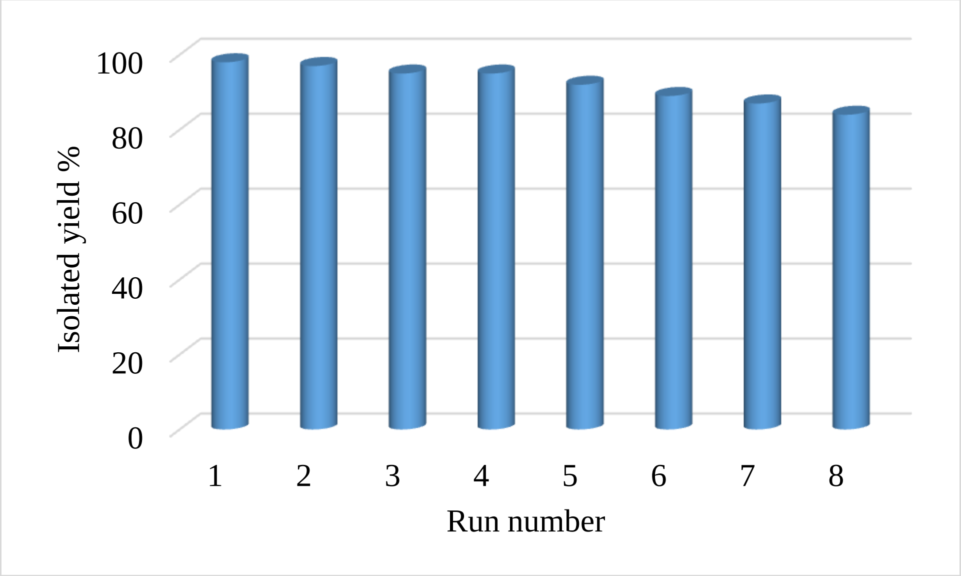


Fig 4. Recyclability of Cu-Adenine@boehmite in the coupling of iodobenzene (1 mmol) with $PhB(OH)_2$ (1 mmol).

3.6. Characterization of recycled catalyst

In order to show the structure stability of Cu-Adenine@boehmite after recycling, recovered catalyst was characterized by XRD technique. The XRD pattern of recovered catalyst was compared to standard XRD pattern of boehmite nanoparticles. The XRD patterns of boehmite nanoparticles and recovered Cu-Adenine@boehmite are shown in Figure 5. As it can be seen, the XRD pattern of recovered catalyst showed a good agreement with standard XRD pattern of boehmite nanoparticles. These results indicate that the crystalline structure of catalyst has not changed after recycling. Therefore, these results are indicates that this catalyst can be reused for next runs without any change in its structure.

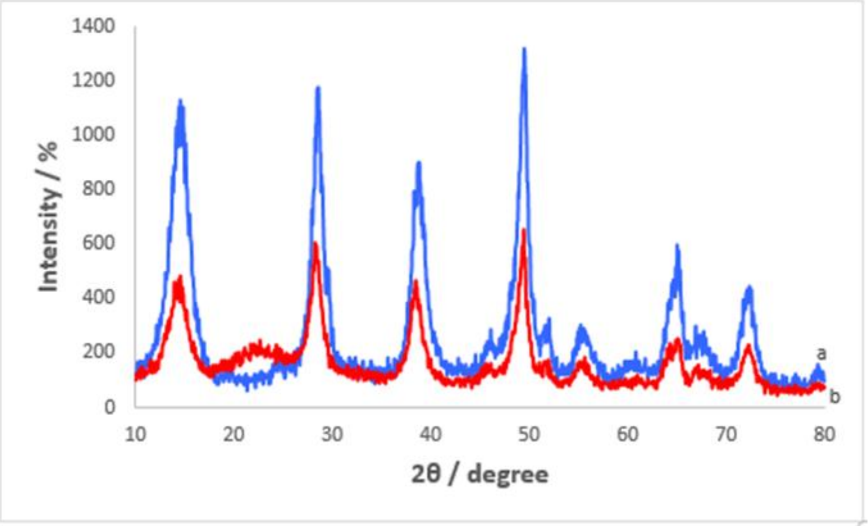


Fig 5. The XRD pattern of boehmite nanoparticles (a) and Cu-Adenine@boehmite after recycling (b).

The particle size of catalyst after recycling has been obtained by SEM technique. The SEM image of recycled Cu-Adenine@boehmite is shown in Figure 6. As shown in figure 6, the size of catalyst after recycling is as same as fresh catalyst, which is about 50-90 nm. As shown in Figure 6, the size and shape of recovered catalyst was shown a good similarly to fresh catalyst.

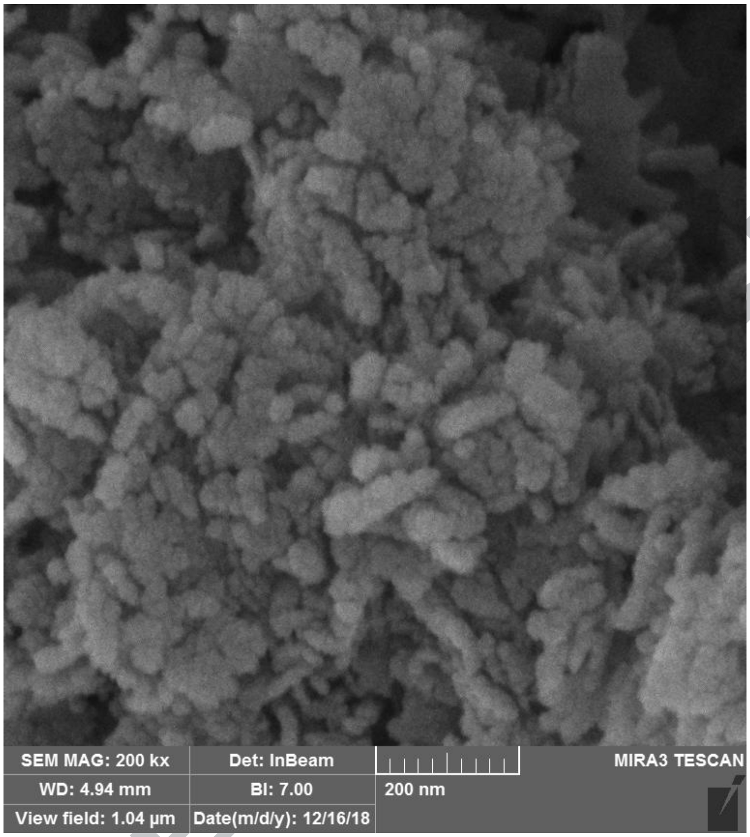


Fig 6. SEM image of Cu-Adenine@boehmite after recycling.

3.7. Leaching study of catalyst

Copper leaching of Cu-Adenine@boehmite was studied by ICP, poisoning test and hot filtration test. Based on ICP-OES analysis, amount of copper in fresh and reused Cu-Adenine@boehmite found to be 0.20×10^{-3} mol g^{-1} and 0.18×10^{-3} mol g^{-1}, respectively, which indicated that metal leaching of this catalyst is very low.

In order to study the heterogeneity of Cu-Adenine@boehmite, hot filtration experiment has been performed in the coupling of iodobenzene with phenylboronic acid. In this study, in half-time of selected reaction, 56% of product was obtained. Then, this reaction was repeated and in half-time of reaction, catalyst was separated and the reaction was then permitted to continue without catalyst for a further 60 min. In this stage, 59% of product was obtained. These experiments confirm that leaching of copper didn't not happened.

3.8. Poisoning test

Poisoning test is a powerful tool for homogeneity/heterogeneity nature of catalytic procedures. Polyvinylpyridine and mercury poisoning tests were often used for extinguishing solution-phase catalysis [63, 64]. In order to study of homogeneity/heterogeneity nature of Cu-Adenine@boehmite, the Suzuki coupling reaction of iodobenzene with phenylboronic acid in the presence of poly(vinyl pyridine) was performed under optimized condition. Therefore, a mixture of iodobenzene (1.0 mmol), phenylboronic acid (1 mmol), Na_2CO_3 (1.5 mmol), water (3 ml), 0.005 g of poly(vinyl pyridine) and Cu-Adenine@boehmite (20 mg, 0.40 mol%) were stirred at 80 °C. In this experiment, considered reaction was completed and any change in conversion was not observed, which proves that Cu-Adenine@boehmite has heterogeneous nature.

Poisoning test, ICP technique and hot filtration test were shown a good agreement for the heterogeneity nature of Cu-Adenine@boehmite.

3.9. Comparison of the Catalyst

The efficiency of Cu-Adenine@boehmite as catalyst was considered by comparing these obtained results with previously reported catalysts in the authentic literatures. Results for synthesis of biphenyls from coupling reaction of aryl halide with phenylboronic acid in the presence of Cu-Adenine@boehmite and previously reported catalysts are summarized in Table 7. Nano-Cu-Adenine@boehmite catalyst has some merits in terms of high yields and shorter reaction times, low reaction temperature, simple catalyst recovering, products purification, and use of green solvent. Also, the TOF and TON numbers in the presence of Cu-Adenine@boehmite are higher than other catalysts, which is confirmed the high efficiency of this catalyst. Therefore, it can be found that Cu-Adenine@boehmite is an efficient catalyst and it is useful in the organic reactions and synthesis of organic compounds. Additionally, Suzuki reaction has usually been reported in the presence of palladium catalyst, which is more expensive than copper catalyst. Also, several procedures used microwave irradiation (Table 7, entries 11-15) or ultrasonic sonication (Table 7, entry 16) in Suzuki coupling reaction to decrease reaction time or improvement of yield.

Table 7. Comparison of Cu-Adenine@boehmite in the coupling reaction of iodobenzene or 4-Iodotoluene with phenylboronic acid with previously reported procedures.

Entry	Catalyst (mol %)	Aryl halide	Reaction conditions	Time (min)	TON	TOF (h^{-1})	Yield ^{a} (%) [Reference]
1	PANI-Pd (2.2 mol%)	Iodobenzene	K_2CO_3, 1,4-dioxane: H_2O (1:1), 95 ºC	240	41	10	91 [65]
2	N,N'-bis(2-pyridinecarboxamide)-1,2-benzene palladium complex (1 mol%)	Iodobenzene	H_2O, K_2CO_3, 100 ºC	180	97	32	97 [66]
3	Pd(II)–NHC complex (1 mol%)	Iodobenzene	DMF, Cs_2CO_3, 100 ºC	24h	99	4	99 [67]
4	NHC-Pd(II) complex (1.0 mol%)	Iodobenzene	THF, Cs_2CO_3, 80 ºC	12h	88	7	88 [68]
5	Pd/Au NPs (4.0 mol%)	Iodobenzene	EtOH/H_2O, K_2CO_3, 80 ºC	24h	22	1	88 [69]
6	Pd NP (1.0 mol%)	Iodobenzene	H_2O, KOH, 100 ºC	12h	95	4	95 [70]
7	CA/Pd(0) (0.5-2.0 mol%)	Iodobenzene	H_2O, K_2CO_3, 100 ºC	120	188	94	94 [71]
8	Polymer anchored Pd(II) Schiff base complex (0.5 mol%)	Iodobenzene	K_2CO_3, DMF: H_2O (1:1), 80 ºC	300	198	40	99 [72]
9	Pd@SBA-15/ILDABCO (0.5 mol%)	Iodobenzene	K_2CO_3, H_2O, 80 ºC	90	194	129	97 [73]
10	SBA-16-2 N-Pd(II) (0.5 mol%)	Iodobenzene	EtOH, K_2CO_3, 60 ºC	120	198	99	99 [74]
11	Pd NPs@APC (1.8×10^{-3} mol%)	4-Iodotoluene	solvent-free, K_2CO_3, MW (350 W)	5	37.2	446	67 [75]

12	AG-Pd (0.003 mol%)	4-Iodotoluene	solvent-free, Cs_2CO_3, MW (400 W), 50 ºC	6	28.3	283	85 [76]
13	CL-Gly-Pt (0.002 mol %)	4-Iodotoluene	solvent-free, K_2CO_3, MW (400 W), 50 ºC	7	30	257	60 [77]
14	Pd nanocatalyst (0.004)	4-Iodotoluene	solvent-free, K_2CO_3, MW (400 W), 50 ºC	5	18	225	72 [78]
15	Pd@chitosan/starch nanocomposite (0.005 mol%)	4-Iodotoluene	solvent-free, K_2CO_3, MW (400 W), 50 ºC	6	15	150	75 [79]
16	Pd NPs@CMC/AG (1 mol%)	4-Iodotoluene	H_2O, K_2CO_3, MW, 60 ºC, ultrasonic sonication	30	75	150	75 [80]
17	Pd(0)-Schif-base@MCM-41 (1.6 mol %)	4-Iodotoluene	PEG, K_2CO_3, 100 ºC	200	61	18	97 [81]
18	Cu-Adenine@boehmite (0.40 mol %)	4-Iodotoluene	H_2O, Na_2CO_3, 80 °C	90	237	158	95 [this work]
19	Cu-Adenine@boehmite (0.40 mol %)	Iodobenzene	H_2O, Na_2CO_3, 80 °C	60	245	245	98 [this work]

4. Conclusion

In conclusion an efficient and reusable heterogeneous catalyst (Cu-Adenine@boehmite) was synthesized and successfully applied for the C-C cross coupling reaction, synthesis of polyhydroquinoline derivatives and selective oxidation of sulfides to sulfoxides. The present methodology offers good turnover numbers (TON) and turnover frequency (TOF) in all reactions. Also, all reaction were carried out in green conditions. Additionally, the Cu-Adenine@boehmite is more economic and environment friendly because of its low Cu leaching. Cu-Adenine@boehmite can be recovered and reused over than 8 times without any significant loss of its activity. Also Cu-Adenine@boehmite is better in terms of facile synthesis of catalyst, price, higher catalytic efficiency, heterogeneous nature, wide substrate scope, and green conditions. Also, Suzuki reaction has usually been reported in the presence of palladium catalyst, but in this work copper catalyst was employed for Suzuki reaction, which Cu catalyst is nontoxic, more inexpensive, easy available and environmental friendly conditions compared with Pd catalyst.

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Modification of boehmite nanoparticles with Adenine for the immobilization of Cu(II): organic-inorganic hybrid nanocatalyst in organic reactions

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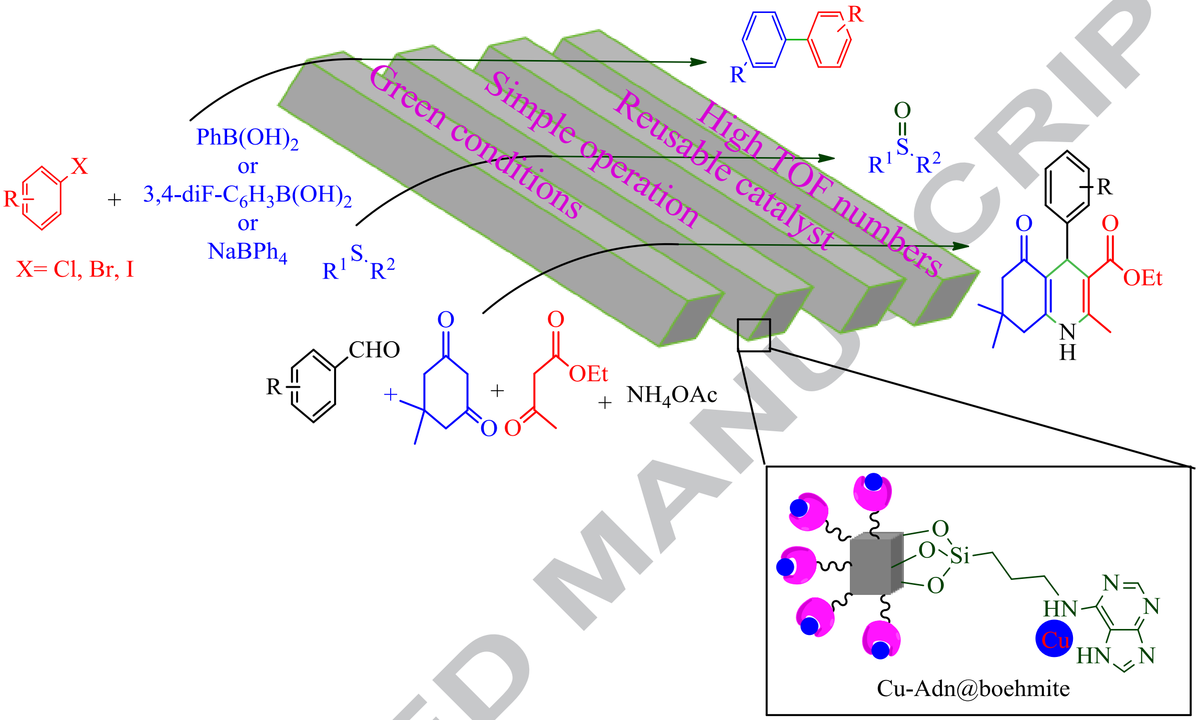

Nanoboehmite was prepared in water at room temperature using commercially available materials. Then copper (II) has been immobilized on its surface and applied as nanocatalyst for the organic reactions under mild conditions. The pure organic products were obtained in high TON and TOF numbers and good yields.