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Highly Water-dispersible Magnetite Nanoparticles Supported-Palladium-β-Cyclodextrin as Efficient Catalyst for Suzuki-Miyaura and Sonogashira Coupling Reaction

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We reported here a novel highly water-dispersible and recoverable magnetite supporting a palladium-β-cyclodextrin complex as an efficient catalyst in Suzuki-Miyaura and Sonogashira carbon-carbon coupling reactions. The magnetite nanoparticles supporting catalyst was characterized by FT-IR, CHN, EDS, TGA, XRD, TEM and VSM. The prepared catalyst displayed excellent activity for wide range of substrates in aqueous solution under mild reaction conditions. The reusability of magnetite supporting palladium-β-cyclodextrin nanocatalyst was successfully examined five times with a slight loss of catalytic activity.

Introduction

Transition metal-catalyzed carbon–carbon bond formation reactions are important methodologies in catalytic coupling reactions because they facilitate key steps in synthesis of many significant products in the commercialized or development phase.[1]

Palladium-catalyzed carbon-carbon coupling of aryl halides/triflates with arylboronic acids as reagents with nontoxic nature, high stability to air, heat and moisture emerged as extremely powerful tools in biaryl synthesis during the past decade. The significant reactions are generally called the Suzuki-Miyaura reaction.[2] In addition to the reaction, palladium-catalyzed Sonogashira coupling is also one of the most important catalytic reactions for the formation of sp^2-sp carbon-carbon coupling between alkenyl or aryl halides/triflates and terminal alkynes.[3]

Improvements in these catalytic coupling reactions have led to a great interest in the increased reactivity and stability of the metal catalysts by use of efficacious supporting ligands such as phosphines[4], N-heterocyclic carbenes[5], Palladacycles[6] and others.[7] However, drawbacks for their attaching and removing, and environmental concerns cause many attempts to overcome these issues. To overcome these problems, many attentions have been directed toward the development of new methods to immobilize the homogeneous palladium catalysts onto various solid supports such as silica[8], metal–organic framework[9], polymers[10] and metal oxides[11] which is easier to separate and recycle the catalyst without much problems of metal pollution in the final products.

In recent years magnetite nanoparticle-supported catalysts have attracted much attention in developing greener catalytic reactions. The magnetite-supported catalysts with high catalytically active surface areas, low porosity and readily dispersed in the reaction system are well accessible to the reactants. Also, magnetic nanoparticles can be simply removed from the reaction medium by an external magnet readily without spending much time and laborious separation steps.[11d, 12]

During the past years, many attempts have been focused on the homogeneous catalysts with water-soluble ligand.[13] Traditional strategy for obtaining a water-soluble catalyst is to modify ligands with a hydrophilic functional group such as sulfonates[14], carboxylates[15], ammonium salts[16] and polyethylene glycol.[17] Although preparation of water dispersible magnetite nanoparticles through surface modification with hydrophilic groups have been pursued by many research groups for bio-related applications[18], the surface-modified magnetite as solid supports with hydrophilic groups have been recently developed by us for Pd-catalyzed coupling reactions in neat water.[19] In our continuous interests in developing a greener metal-catalyzed reaction, we have also focused on β-cyclodextrin (β-CD) as a greener supramolecular compound.

β-CD is a water-soluble, low price and semi natural cyclic oligosaccharide possessing a hydrophobic cavity that can bind substrates selectively. The reversible formation of the host–guest complexes by non-covalent bondings in the cavity could be a good chance for catalytic reactions upon installation of transition metals to the cavity.[20] Consequently, catalytic coupling reactions on the basis of this green supramolecular have been the focus of many investigations.[21] In this context, we have also developed the Cu^{II}-β-Cyclodextrin complexes which work as homogeneous or heterogeneous catalyst in homo- and cross-coupling of arylboronic acids.[22]

Due to importance of heterogeneous catalyst from environment concerns, specifically magnetically separable catalyst in water without use of any additives such as phosphine ligand or phase transfer reagent,[23] we have designed and synthesized the hydrophilic Pd^{II}-β-Cyclodextrin complex (MNP-CD-Pd) anchored on 3-aminopropyltriethoxysilane-functionalized magnetite

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nanoparticles as a highly water dispersible heterogeneous catalyst having the hydrophobic cavity for carbon-carbon coupling reaction in aqueous solutions**.** In this paper we now disclose the characterization and reactivity of MNP-CD-Pd directing toward the Suzuki-Miyaura coupling reaction and the Sonogashira reaction.

Experimental

General

All reagents and solvents were purchased from commercial suppliers. NMR spectra were recorded at 25°C on a Bruker Avance 400 NMR Spectrometer (^{1}H NMR: 400 MHz; ^{13}C NMR: 100 MHz). Gas chromatography was performed with a Varian CP 3800 chromatograph. Analytical TLC was carried out with Merck plates precoated with silica gel 60 F254 (0.25 mm thick). Thermogravimetric analysis was conducted from room temperature to 800 °C in an oxygen flow using a NETZSCH STA 409 PC/PG instrument. A Varian spectrum 110 atomic absorption spectrometry was used to investigate the content of palladium in the catalyst. FT-IR spectra were obtained using a Bruker Vector 22 instrument with samples prepared as KBr pallets. The magnetic properties of the prepared magnetite nanoparticles were measured with a Vibrating Sample Magnetometer (Meghnatis Daghigh Kavir Company, Iran) at room temperature from −10 000 to +10 000 Oe. Transmission electron microscopy (Philips CM30 TEM) and powder X-ray Diffraction pattern were used to investigate the structure and morphology of the prepared materials. Elemental analyses were performed by the Elemental Vario EL III.

Synthesis of Palladium-β-Cyclodextrin complex

Palladium-β-Cyclodextrin (Pd^{II}-β-CD) complex was prepared in an analogues manner for previous preparation of Cu^{II}-β-CD with slight modification.[22a] Palladium acetate (3 mmol, 0.673 g) was added to a solution of NaOH (0.5 M, 50 mL) and β-cyclodextrin (1 mmol, 1.135 g). The mixture was stirred at ambient temperature for 12 h and a light yellow solution was prepared after dissolving the palladium acetate. After 12 h ethanol (500 mL) was added to this solution until the light yellow suspension was formed. Then these precipitates were filtrated and washed with ethanol and air-dried at ambient temperature. The prepared Pd^{II}-β-CD complex was characterized by atomic absorption, EDS and ^{1}H NMR (see supporting information), which confirmed the presence of palladium in the complex.

Preparation of mono-6-*O*-(*p*-toluenesulfonyl)-Palladium-β-Cyclodextrin (Ts-Pd-β-CD)

Pd^{II}-β-CD (1 g) was dissolved in 20 mL of sodium hydroxide solution (0.5 M). *p*-Toluenesulfonyl chloride (0.95 g, 5 mmol) was added to that solution and the mixture was stirred at room temperature for 4h. After 4 h reaction mixture filtrated and 500 mL ethanol was added to filtrated solution to precipitate Ts-Pd-β-CD. The resulting precipitate was filtered and dried in vacuum oven.[21i,24] Appearance of aromatic hydrogen peaks in ^{1}H NMR in D_2O confirmed successfully tosylation of Pd^{II}-β-CD complex.

Preparation of Fe_3O_4 nanoparticles (MNP)

The magnetite nanoparticles were prepared by traditional chemical co-precipitation method.[25] $FeCl_3.6H_2O$ (2.36 g) and $FeCl_2.4H_2O$ (0.86 g) were dissolved in 40 mL distilled water under stirring at 90 °C and continuous flow of argon gas. Subsequently, 10 mL of ammonia (25%) was added drop-wise to the reaction mixture with intense stirring. Prepared nanoparticles were magnetically separated and washed with deionized water repeatedly and dried in vacuum oven. FT-IR (KBr, cm^{-1}): 570, 1123, 1624, 3400 cm^{-1}.

Functionalization of Fe_3O_4 with 3-aminopropyltriethoxysilane (MNP-AP)

Magnetite nanoparticles (MNP, 1g) were dispersed in dry toluene (20 mL) by sonication for 30 min and then 3-aminopropyltriethoxysilane (APTES, 2 mL) was added to the resulting mixture. The mixture was refluxed for 24 h under argon atmosphere. After 24 h, the functionalized magnetite nanoparticles (MNP-AP) were separated by an external magnet, washed thoroughly with ethanol and distilled water, and dried under vacuum oven. FT-IR (KBr, cm^{-1}): 570, 1050, 1123, 2917, 1560, 3400 cm^{-1}.

Preparation of MNP-CD-Pd catalyst

For preparation of magnetite supported palladium-β-cyclodextrin catalyst (MNP-CD-Pd), MNP-AP (0.5 g) was dispersed in DMF (10 mL) for 30 min using ultrasound. Ts-Pd-β-CD (50 mg) was added to the mixture and the mixture was stirred at 80 °C for 24 h. After 24 h MNP-CD-Pd was separated by an external magnet and repeatedly washed with distilled water/ethanol and then dried under vacuum oven. FT-IR (KBr, cm^{-1}): 580, 1031, 1156, 1250, 2926, 3406 cm^{-1}.

General procedure for Suzuki-Miyaura coupling reaction with MNP-CD-Pd catalyst

To a mixture of MNP-CD-Pd (0.03-0.15 mol% based on palladium) and K_2CO_3 (0.30 mmol) in water (2 mL), aryl halide (0.2 mmol) and arylboronic acid (0.24 mmol) were added and the mixture was stirred at reflux condition at 100 °C. The reaction progress was monitored by TLC and GC until the completion of the reaction. Then, the product was extracted by n-Hexane (2×3 mL). The combined organic phases were concentrated. The residue was purified with column chromatography to give coupling product, which was characterized with ^{1}H and ^{13}CNMR. MNP-CD-Pd remaining in aqueous phase was separated by an external magnet, washed thoroughly with ethanol and distilled water and dried under vacuum oven. All coupling products gave satisfactory spectral data in accord with the assigned structures. For example: **3a:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 3.89 (3H, s), 7.01 (2H, d), 7.33 (1H, t), 7.45 (2H, t), 7.55 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 55.4, 114.2, 126.7, 126.7, 128.2, 128.7, 133.8, 140.8, 159.1. **3b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.39 (2H, t), 7.49 (4H, t), 7.65 (4H, d). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 127.2, 127.3, 128.8, 141.2.

General procedure for Sonogashira coupling reaction with MNP-CD-Pd catalyst

To a mixture of MNP-CD-Pd (0.075-0.15 mol% based on palladium) and K_2CO_3 (0.40 mmol) in 2 mL H_2O/DMF, aryl halides (0.20 mmol) and terminal alkyne (0.24 mmol) were added, and stirred at 100-120 °C. The reaction progress was monitored by TLC and GC. After completion of the reaction, the product was extracted by ethyl acetate (2x3 mL). The combined organic phases were concentrated. The residue was purified with column chromatography to give coupling products, which were characterized with ^{1}H and ^{13}C NMR. MNP-CD-Pd remaining in aqueous phase was separated by an external magnet, washed thoroughly with ethanol and distilled water and dried under vacuum oven. All coupling products gave satisfactory spectral data in accord with the assigned structures. For example: **6a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.29-7.42 (6H, m), 7.56-7.59 (4H, m) ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm) = 89.40,

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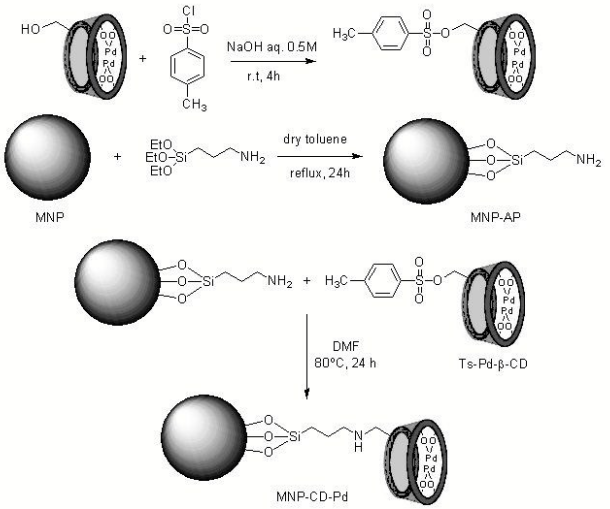
123.30, 128.28, 128.37, 131.64. **6b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.40 (3H, s), 7.19 (2H, d), 7.35-7.37 (3H, 3), 7.46 (2H, d), 7.53-7.55 (2H m). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 21.54, 88.73, 89.57, 120.20, 123.50, 128.10, 128.34, 129.19, 131.52, 131.57, 138.41.

Results and discussion

The magnetite nanoparticle-supported Pd-β-Cyclodextrin catalyst prepared with following the procedure that shown in Scheme 1. Firstly Pd-β-Cyclodextrin complex was prepared by as same procedure for the preparation of Cu^{II}-β-CD.[22a] The complex formation of the Pd(II) with β-cyclodextrin was also estimated by the ^{1}H NMR analysis of Pd(II)-β-CD complex. As shown in Figure s2, the ^{1}H NMR (400 MHz) of the complex shows significant signal broadening as a consequence of the presence of Pd(II) bonded to β-cyclodextrin. The line broadening is particularly for the multiplets signals corresponding to the OH groups bonded to carbons 2, 3 and 6 at 5.70 and 4.45 ppm. The complex was tosylated using *p*-toluenesulfunyl chloride in sodium hydroxide solution readily.[21i] Secondly, magnetite nanoparticles (MNP) prepared with co-precipitation of Fe salts with ammonia and functionalized with 3-aminopropyltriethoxysilane (MNP-AP).[25] Finally, MNP-CD-Pd was prepared by a simple condensation between MNP-AP and Ts-Pd-β-CD. The supported catalyst can be homogeneously dispersed in water to produce a brown solution. The prepared catalyst was characterized by FT-IR, CHN, EDS, TGA, XRD, TEM, VSM and atomic absorption spectrometry.



Scheme 1 Schematic route for the Preparation of MNP-CD-Pd

Figure 1 shows FT-IR spectra for magnetite nanoparticle and functionalized nanoparticles. It shows sharp peak at 570 cm^{-1} correspond to the Fe-O stretching frequency and a strong broad band at 3400 cm^{-1} is assigned hydroxyl stretching vibration for MNP (Figure 1a). Appearance absorption bands at 2917 cm^{-1} (aliphatic C-H groups) and at 1050 cm^{-1} (Si-O group) in MNP-AP spectra indicate magnetite nanoparticles functionalization has been done successfully (Figure 1b). For MNP-CD-Pd spectra additional peak at 1215 cm^{-1} and increase absorption intensity of aliphatic C-H groups confirm immobilization of Pd-β-CD on the magnetite nanoparticles successfully.

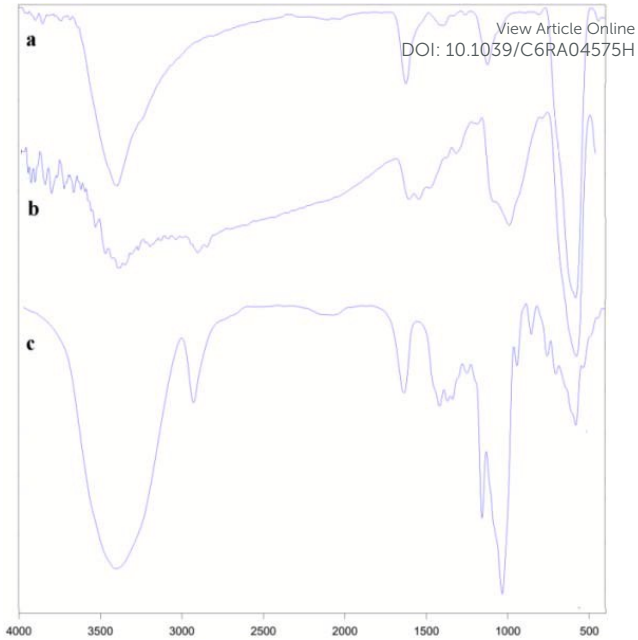


Figure 1 FT-IR spectra (a) MNP (b) MNP-AP (c) MNP-CD-Pd

Also, elemental analysis (Table 1) for MNP-AP and MNP-CD-Pd confirm successfully grafting of organic groups on manganite nanoparticles surface. The content of Pd in MNP-CD-Pd was measured by atomic absorption spectrometry (0.062 mmol of pd per one gram of the catalyst). Moreover, the electron-dispersive X-ray (EDS) spectrum exhibited the presence of carbon, silicon and specially palladium in the structure of MNP-CD-Pd catalyst that confirmed catalyst preparation successfully (Figure 2).

Table 1 Elemental analysis

Nanoparticles	N (Weight%)	C (Weight%)	H (Weight%)
MNP-AP	2.471	7.041	1.623
MNP-CD-Pd	2.155	8.059	1.326

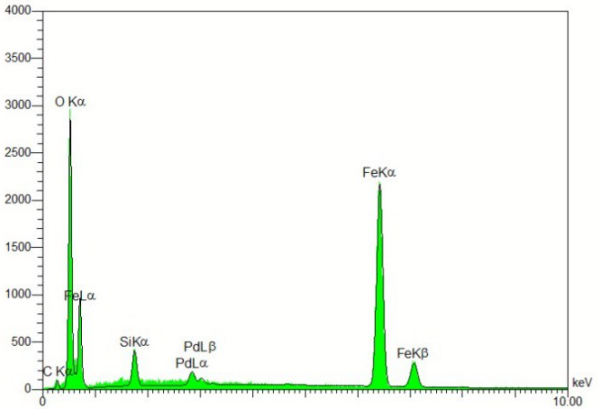


Figure 2 EDS spectrum of prepared MNP-CD-Pd catalyst

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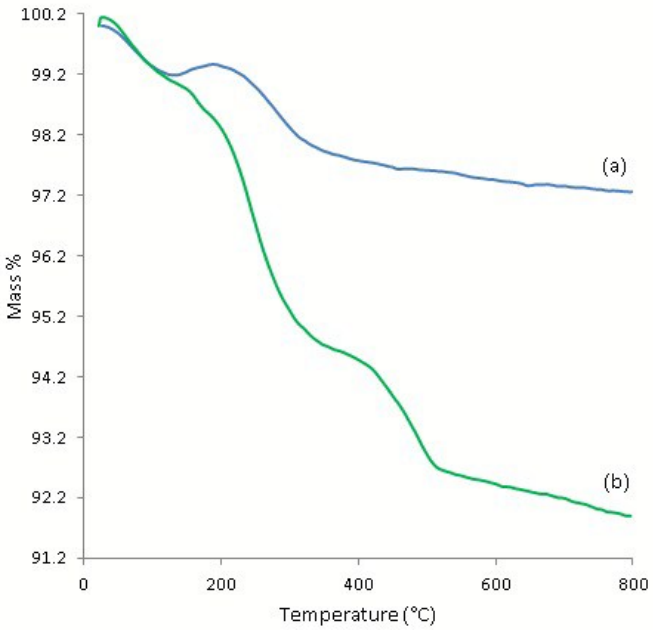

Figure 3 Thermogravimetric analysis (a) MNP (b) MNP-CD-Pd

Thermogravimetric analysis (TGA) of MNP and MNP-CD-Pd (Figure 3) was proved the presence of aminopropyl and β-cyclodextrin on the surface of magnetite nanoparticles. According to TG analysis, the total weight loss of MNPs over the full temperature range of 30–400°C was estimated to be 2.0 wt% due to the loss of the adsorbed water as well as dehydration of the surface OH groups (Figure 3a). For MNP-CD-Pd the TGA curve shows two considerable weight loss steps that second step in the range of 400-520 °C related to β-cyclidextrin decomposition (Figure 3b).

Structure and morphology of the catalyst was determined by X-Ray reflective diffraction (XRD) and transmission electron microscopy (TEM). The TEM image in Figure 4 shows that the MNP-CD-Pd nanoparticles are of nearly spherical shape with mean diameter of about 25 nm.

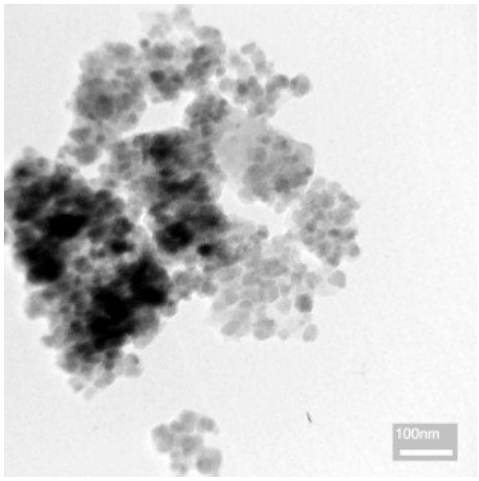

Figure 4 TEM images of MNP-CD-Pd

The XRD patterns (Figure 5) of MNP, MNP-AP and MNP-CD-Pd exhibits diffraction peaks corresponding to the standard spinel cubic Fe_3O_4 pattern (JCPDS card No. 79-0417) and no peaks characteristic for palladium nanoparticles were observed in MNP-CD-Pd. The average crystallite sizes estimated using Scherrer's equation is ~13 nm for MNP-CD-Pd.

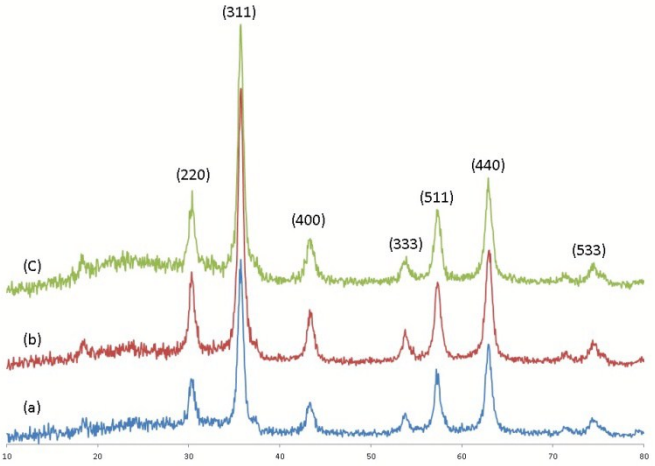

Figure 5 XRD patterns of (a) MNP (b) MNP-AP (c) MNP-CD-Pd

The magnetic properties of nanoparticles were investigated with a Vibrating Sample Magnetometer (VSM). Figure 6 shows the magnetic hysteresis loops of MNP, MNP-AP and MNP-CD-Pd in an applied magnetic field of 10000 Oe at room temperature. Prepared magnetite nanoparticles show superparamagnetic behavior with no remaining effect from the hysteresis loops with removing the applied magnetic field. However functionalization of nanoparticles (MNP-AP and MNP-CD-Pd) affected the saturation magnetization of these magnetite nanoparticles, because of the two coating layers of APTES and Pd-β-Cyclodextrin.

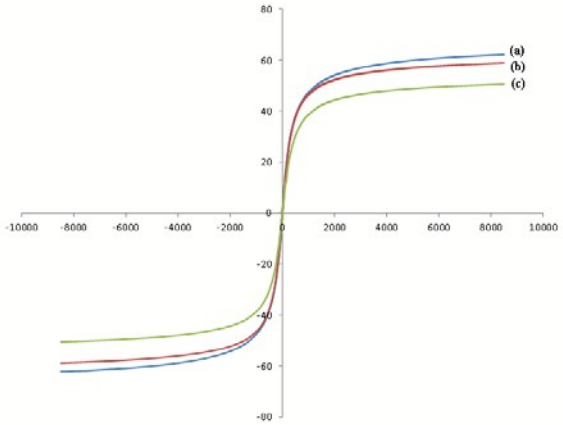

Figure 6 Magnetic hysteresis loops of (a) MNP (b) MNP-AP (c) MNP-CD-Pd

The catalytic behavior of prepared MNP-CD-Pd was investigated for the synthesis of biaryls from aryl boronic acids and aryl halides (Suzuki-Miyaura reaction). The reaction of 4-bromoanisole and phenyl boronic acid was used as model reaction for optimization of Suzuki-Miyaura coupling reaction (Table 2). At the outset, commonly utilized bases were tested with 0.15 mol% of the catalyst in water at 100 °C for 4h (entry 1-8). The best result was observed for K_2CO_3 in water (entry 3). Subsequently, we try to decrease catalyst amount and temperature, but we weren't found promising

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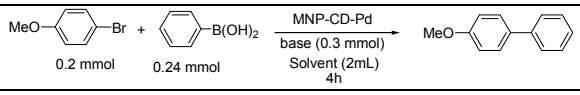
results (entry 9-13). So, K_2CO_3 base in water and 0.15 mol% of the catalyst at 100 °C for 6 h selected as an optimal reaction condition.

Table 2 Optimization of the Suzuki-Miyaura coupling reaction in the presence of MNP-CD-Pd



Entry	Base	Solvent	Cat. (mol%)[a]	T (°C)	Yield (%)[b]
1	NaOH	H_2O	0.15	100	69
2	Cs_2CO_3	H_2O	0.15	100	71
3	K_2CO_3	H_2O	0.15	100	87
4	Na_2CO_3	H_2O	0.15	100	16
5	K_3PO_4	H_2O	0.15	100	63
6	Et_3N	H_2O	0.15	100	52
7	K_2CO_3	H_2O/MeOH	0.15	reflux	70
8	K_2CO_3	H_2O/DMF	0.15	100	67
9	K_2CO_3	H_2O	0.075	100	75
10	K_2CO_3	H_2O	0.03	100	76
11	K_2CO_3	H_2O	0.015	100	55
12	K_2CO_3	H_2O	0.15	80	60
13	K_2CO_3	H_2O	0.15	60	18
14[c]	K_2CO_3	H_2O	0.15	100	96

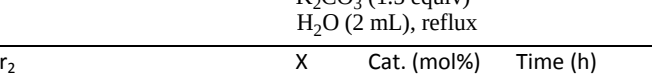
a) 1 mg Cat. = 0.03 mol% Pd for 0.2 mmol arylhalide, b) GC yield
c) 6h

The homo-coupling of boronic acid as byproduct was not significant under this condition.

Under the above optimized conditions, cross-coupling reaction of aryl halides with large scope of aryl boronic acids was studied in the presence of MNP-CD-Pd catalyst (0.03-0.3 mol% Pd) (Table 3). In general, most of the products were obtained in good to excellent yield with high TONs within 4-24 h. As expected aryl iodides and bromides react efficiently with aryl boronic acids in the presence of MNP-CD-Pd (0.03-0.15 mol% of the catalyst) whitin 4-12 h (Table 3, entry 1-25). MNP-CD-Pd catalyst shows high selectivity for 1-chloro-4-iodo-benzene (entry 10). Treatment of aryl halides with a variety of electron-withdrawing, electron-donating groups and heteroaryl compounds of arylboronic acids gave the corresponding products in good to high yield. Electron-withdrawing functional groups in aryl halides increase the reactivity and electron-donating groups decrease the reactivity. Treatment of 2-substituted aryl iodide with phenyl boronic acid (entry 11) gives the corresponding biaryl in high yield, but treatment of iodobenzene with 2,6-dimethylphenyl boronic acid (entry 8) gave only 10% of desired product after 24 h in 0.15 mol% of the catalyst. There was no reaction when the less reactive aryl chlorides were used (not shown in table) in the coupling reaction with arylboronic acids, while the reaction proceeded with adding of 0.5 equiv of TBAB (tetra butyl ammonium bromide) as a phase transfer catalyst (entries 26-28).[19]

Len et al. reported that the addition of arylboronic acids to Pd(II) in

Table 3 The Suzuki-Miyaura coupling reaction of various aryl halides and boronic acids in the presence of MNP-CD-Pd catalyst



Entry	Ar_1	Ar_2	X	Cat. (mol%)	Time (h)	Yield[a] (%)	Product
1	Ph	Ph	I	0.03	4	96	3b
2	Ph	4-Me-C_6H_4	I	0.03	4	100	3c
3	Ph	4-OMe-C_6H_4	I	0.03	4	100	3a
4	Ph	3-NO_2-C_6H_4	I	0.075	8	98	3d
5	Ph	3,5-difluoro-C_6H_3	I	0.03	4	99	3e
6	Ph	2-Benzofuranyl	I	0.03	6	100 (84)[b]	3f
7	Ph	2-Naphtyl	I	0.03	6	100 (89)[b]	3g
8	Ph	2,6-dimethyl-C_6H_3	I	0.15	24	10	3h
9	Ph	1-Naphtyl	I	0.075	8	99	3i
10	4-Cl-C_6H_4	Ph	I	0.03	6	98	3j
11	2-Me-C_6H_4	Ph	I	0.075	6	99	3k
12	4-NO_2-C_6H_4	Ph	I	0.03	4	98	3l
13	4-CHO-C_6H_4	Ph	Br	0.03	4	98	3m
14	Ph	Ph	Br	0.03	4	71	3b
15	4-CHO-C_6H_4	4-Me-C_6H_4	Br	0.03	4	100	3n
16	4-CHO-C_6H_4	4-OMe-C_6H_4	Br	0.03	4	100	3o
17	Ph	4-Me-C_6H_4	Br	0.06	6	100	3c
18	Ph	4-OMe-C_6H_4	Br	0.06	6	84	3a
19	4-OMe-C_6H_4	Ph	Br	0.15	6	96	3a
20	4-OMe-C_6H_4	3,5-difluoro-C_6H_3	Br	0.075	8	98	3p
21	4-OMe-C_6H_4	4-Me-C_6H_4	Br	0.15	8	84[b]	3q
22	4-OMe-C_6H_4	4-OMe-C_6H_4	Br	0.15	8	75[b]	3r
23	4-OMe-C_6H_4	2-Benzofuranyl	Br	0.075	12	75[c] (63)[b]	3s
24	4-OMe-C_6H_4	2-Naphtyl	Br	0.15	8	83[b]	3t
25	5-Pyrimidine	Ph	Br	0.03	8	91	3u
26[d]	4-CHO-C_6H_4	Ph	Cl	0.3	24	62	3m
27[d]	4-NO_2-C_6H_4	Ph	Cl	0.3	24	65	3l
28[d]	Ph	Ph	Cl	0.3	24	36	3b

a) GC yield, b) Isolated yield, c) H NMR yield, d) H_2O/DMF (1:1) as a solvent and 0.5 eq. TBAB

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water as a solvent afforded Pd(0) species.[21n] It is suggested that Pd(II) in MNP-CD-Pd catalyst is reduced in situ in the presence of arylboronic acids to form catalytically Pd(0) species on the surface of MNP-CD. A proposed mechanism is outlined in Figure 7 for the Suzuki-Miyaura coupling reaction of various aryl halides and boronic acids in the presence of MNP-CD-Pd catalyst.

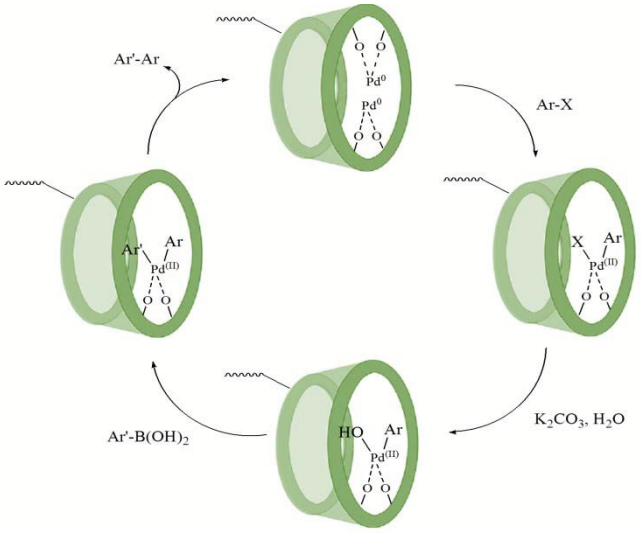
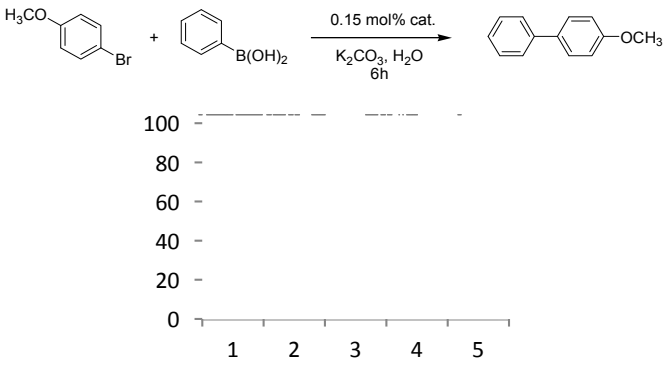


Figure 7 Proposed mechanism for the Suzuki-Miyaura coupling reaction of various aryl halides and boronic acids in the presence of MNP-CD-Pd catalyst

The recyclability and reusability are very important points for heterogeneous catalysis systems. So the reusability of MNP-CD-Pd catalyst in the model reaction (reaction of 4-bromoanisole with phenylboronic acid) was investigated. The reusability experiments results showed that catalytic activity did not decrease considerably after four catalytic cycles (Figure 8). Atomic absorption analysis of recovered catalyst showed that Pd amount decreased to 0.030 mmol of pd per gram of MNP-CD-Pd after fifth run. The EDS analysis of recycled catalyst confirmed the presence of palladium in the reused catalyst after fifth run (Figure s14). Thermogravimetric analysis for recovered MNP-CD-Pd after fifth run showed that



Run	1	2	3	4	5	Average
Yield	96	95	97	90	80	91

Figure 8 Reusability test for MNP-CD-Pd in the Suzuki–Miyaura coupling reaction

Table 4 optimization of sonogashira coupling reaction of iodobenzene and phenylacetylene in the precence MNP-CD-Pd

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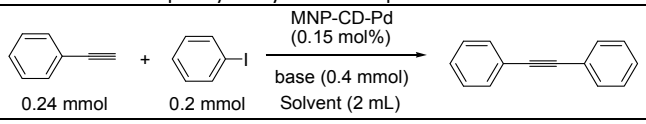

	Base	Solvent	T (°C)	Time (h)	Yield (%)[b]
1	K_2CO_3	H_2O	100	6	43
2	K_2CO_3	H_2O/EtOH (1:1)	100	6	37
3	K_2CO_3	H_2O/DMF (3:1)	100	6	95
4	NaOH	H_2O/DMF (3:1)	100	6	52
5	Cs_2CO_3	H_2O/DMF (3:1)	100	6	90
6	Na_2CO_3	H_2O/DMF (3:1)	100	6	51
7	K_3PO_4	H_2O/DMF (3:1)	100	6	74
8	Et_3N	H_2O/DMF (3:1)	100	6	58
9	DABCO	H_2O/DMF (3:1)	100	6	90
10[c]	K_2CO_3	H_2O/DMF (3:1)	100	6	96
11	K_2CO_3	H_2O/DMF (3:1)	60	24	74

a) 1mg Cat. = 0.03 mol% for 0.2 mmol arylhalide, b) GC yield, c) 0.075 mol% catalyst

catalyst is still stable and organic layers were present on the surface of the catalyst (Supporting Information).

To the further study on other application of novel prepared catalyst, we studied the Sonogashira catalytic coupling reaction of aryl iodides and bromides with terminal alkynes in the presence of MNP-CD-Pd catalyst. In order to obtain optimized reaction condition, treatment of iodobenzene with phenylacetylene in aqueous solution chosen as the model reaction in various reaction conditions. The results are summarized in Table 4. The results showed that K_2CO_3 as a base is a convenient base for Sonogashira coupling reaction of iodobenzene with phenylacetylene in a solvent mixture of H_2O/DMF (3:1) at 100 °C using 0.15 mol% of the catalyst (entry 3). Further investigations showed that no decrease in the reaction yield was observed with decreasing of the catalyst loading to 0.075 mol% (entry 10). So K_2CO_3 as a base in H_2O/DMF as solvent in the presence of 0.075 mol% of the catalyst at 100 °C chosen as optimized reaction conditions.

With having optimized condition, the feasibility of Sonogashira cross coupling reaction of aryl halides with terminal alkynes in the presence of MNP-CD-Pd catalyst (0.075-0.15 mol%) was studied and the results are summarized in Table 5.

As indicated in Table 5, it is observed that the catalytic system is efficient in the coupling of alkynes with aryl iodides bearing electron-donating and electron-withdrawing functional groups (entries 1-10). According to the results of table 4 electron-withdrawing functional groups in aryl iodide increase reactivity (entries 3 and 4) related to electron-donating functional groups (entries 8 and 9). Also, reaction of aryl bromides with electron withdrawing groups proceeded very well and the desired products were obtained in excellent yields (entries 14 and 16).

Conclusion

In conclusion, we have developed a new, efficient, greener and easily recoverable heterogeneous magnetite nanocatalyst for Suzuki-Miyaura and Sonogashira carbon-carbon coupling reaction in aqueous solution. The heterogeneous magnetite nanocatalyst for the coupling reactions is promoted by a novel highly water-dispersible magnetite supported palladium-β-

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Table 5 The Sonogashira coupling reaction of various aryl halides and terminal alkynes in the presence of MNP-CD-Pd catalyst

Entry	Ar_1	Ar_2	X	Cat. (mol%)	Time (h)	Yield[a] (%)	Product
1	Ph	Ph	I	0.075	6	96	6a
2	Ph	4-Me-C_6H_4	I	0.075	3	98	6b
3	4-NO_2-C_6H_4	Ph	I	0.075	6	100	6c
4	4-CN-C_6H_4	Ph	I	0.075	6	100	6d
5	4-Cl-C_6H_4	Ph	I	0.075	6	>99	6e
6	2-thiophene	Ph	I	0.075	4	97	6f
7	2-thiophene	4-Me-C_6H_4	I	0.075	3	96	6g
8	4-OMe-C_6H_4	Ph	I	0.15	6	86	6h
9	4-Me-C_6H_4	Ph	I	0.15	6	97	6b
10	2-Me-C_6H_4	Ph	I	0.075	12	96	6i
11	4-CHO-C_6H_4	Ph	Br	0.15	9	90	6j
12[b]	Ph	Ph	Br	0.15	9	75	6a
13[b]	Ph	4-Me-C_6H_4	Br	0.15	12	85	6b
14	4-NO_2-C_6H_4	Ph	Br	0.15	6	93	6c
15[b]	1-Naphtyl	Ph	Br	0.15	15	97	6k
16	4-CN-C_6H_4	Ph	Br	0.15	9	95	6d
17	5-pyrimidine	Ph	Br	0.075	6	97	6l
18	5-pyrimidine	4-Me-C_6H_4	Br	0.075	4	97	6m
19[b]	4-Me-C_6H_4	Ph	Br	0.15	12	82	6b

[a] GC yield, [b] H_2O/DMF 1:1 and 120 °C

cyclodextrin complex that displayed excellent activity for wide range of substrates in aqueous solution under mild reaction conditions. The reusability of magnetite supported palladium-β-cyclodextrin nanocatalyst was successfully examined five times with very slight loss of catalytic activity.

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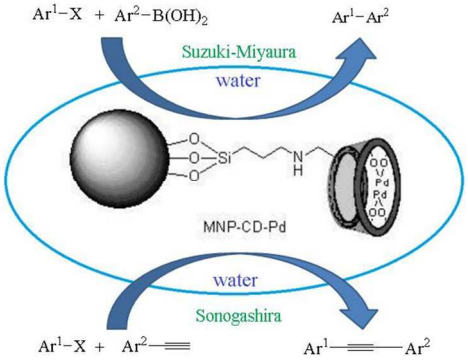

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