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Magnetic MCM-41 nanoparticles as support for the immobilization of organometallic catalyst of palladium and its application in C-C coupling reactions

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In this work, surface of magnetic MCM-41 nanoparticles (MCM-41/Fe₃O₄) modified by 3aminopropyltriemtoxysilane (APTES) and further 1-methyl imidazole was anchored on its surface using cyanuric chloride as linker. Then, Pd^{2+} ions were immobilized on the surface of modified MCM-41/Fe₃O₄ (Pd-imi-CC@MCM-41/Fe₃O₄) and further its application was studied as magnetically recyclable nanocatalyst in carbon-carbon coupling reactions between wide range of aryl halides and butyl acrylate, methyl acrylate, acrylonitrile, phenylboronic acid, or 3,4diflorophenylboronic acid under phosphine-free ligand and air atmosphere. This catalyst has advantages of both Fe₃O₄ nanoparticles and mesoporous MCM-41. Catalyst structure was characterized using TEM, SEM, EDS, WDX, N₂ adsorption-desorption isotherms, XRD, TGA, FT-IR, and AAS techniques. Also, recovered catalyst was characterized by SEM, AAS and FT-IR techniques. All products from carbon-carbon coupling reaction were obtained with excellent yields and high TON and TOF values, which were indicate the high efficiency and activity of this catalyst. Selectivity of this catalyst was studied in various aryl halides which are bearing different functional groups. Heterogeneity and stability of Pd-imi-CC@MCM-41/Fe₃O₄ was studied by AAS technique, leaching test and poisoning test. Therefore, this heterogeneous catalyst can be reused for several times.

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1 Introduction

In recent years, a rapid growth in the development of novel supported materials (such as supported catalysts and reagents) were extended in various fields of chemistry, medicine, and biology sciences and especially in catalysis field [1-7]. Designing and preparation of heterogeneous catalysts by immobilization of homogenous species on solid supports is one of the important routes for the developing of novel and efficient catalytic protocols [8-13]. According to green chemistry concept, magnetic nanoparticles (MNPs) and mesoporous materials are as outstanding heterogeneous support in catalytic transformations [14-16]. Magnetic nanoparticles such as Fe₃O₄ have a wide range of unique features such as easy preparation and functionalization, air stability, nontoxicity, moisture resistance and especially facile removing with assistance of external magnet from the reactions mixture [17-25]. However, the major disadvantages of magnetic nanoparticles are low surface area and low durability. On the other hand, mesoporous materials such as MCM-41 have a wide range of unique features such as considerable durability, high specific surface area, air tolerance, large and uniform pore size, high thermal and mechanical stability [26-29]. However, the major disadvantages of mesoporous materials are time consuming, difficulty, and expensive conventional work-up procedures, such as centrifugation or filtration. In order to combine advantages of both magnetic nanoparticles and mesoporous materials, Fe₃O₄ was doped into mesoporous channels of MCM-41, which led to magnetic MCM-41 nanoparticles. Fe₃O₄/MCM-41 has a large surface area, which can be recovered and reused using external magnet and can be considered as ideal and excellent support for catalytic applications. In this regards, we are reporting a new phosphine-free complex of palladium on magnetic MCM-41 nanoparticles as efficient and reusable nanocatalyst for the C-C coupling reactions. Because C-C coupling reactions are powerful methods in modern synthetic of organic chemistry for the preparation of natural products, agrochemicals,

biologically active compounds, pharmaceuticals, hydrocarbons, polymers, and advanced materials [30-41]. Traditionally, palladium-phosphine complexes are highly efficient catalysts for the formation of carbon-carbon bonds [42, 43]. However, phosphorous ligands suffer from several drawbacks such as thermal instability, toxicity, expensive and non-recoverability.

2 Results and discussion

2.1 Catalyst preparation

In the first step, Pd-imi-CC@MCM-41/Fe₃O₄ was prepared based on Scheme 1. Initially, the hydroxyl groups on the surface of Fe₃O₄ nanoparticles were functionalized and coated by silica layer [44] and further these nanoparticles were doped in MCM-41 skeleton to prepare magnetic MCM-41 nanoparticles $(MCM-41/Fe_3O_4)$ [45]. At next step, MCM-41/Fe₃O₄ nanoparticles were modified by (3aminopropyl)triethoxysilane. Subsequently, the amino groups were reacted with cyanuric chloride, followed by reaction with 1-methylimidazole to synthesis imi-CC@MCM-41/Fe₃O₄ [46]. In final step, palladium particles have been immobilized on imi- $CC@MCM-41/Fe_3O_4.$ This resulting nanomaterial characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), energydispersive X-ray spectroscopy (EDS), wavelength dispersive X-ray spectroscopy (WDX), N₂ adsorptiondesorption isotherms. X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), and atomic absorption spectroscopy (AAS) techniques.

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Scheme 1. Synthesis of Pd-imi-CC@MCM-41/Fe₃O₄.

2.2 Catalyst characterization

The particles size and morphology of Pd-imi-CC@MCM-41/Fe₃O₄ were studied by scanning electron microscopies (SEM) technique. SEM image of this catalyst are shown in Figure 1. Uniform and nearly spherical nanoparticles of Pd-imi-CC@MCM-41/Fe₃O₄ are shown in SEM image. SEM image was confirmed that particles of catalyst were prepared nanometer scale.

Also, TEM images of Pd-imi-CC@MCM-41/Fe $_3O_4$ shown in Figure 2. As it can be seen the catalyst was obtained with average size of less than 100.

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Figure 2. TEM images of Pd-imi-CC@MCM-41/Fe₃O₄.

In order to determine the elements content of Pd-imi-CC@MCM-41/Fe₃O₄, EDS analysis was performed (Figure 3). As depicted, the EDS result shows the presence of iron, oxygen, silica, carbon, nitrogen, chlorine and as well as palladium species in described nanomaterial, which is in good agreement with the content of the final catalyst. WDX analysis (X-Ray Mapping) of Pd-imi-CC@MCM-41/Fe₃O₄ is shown in Figure 4. This analysis exhibits homogeneous distributions of iron, oxygen, silica, carbon, nitrogen, chlorine and palladium in the structure.

Also, the exact amount of palladium content of Pd-imi-CC@MCM-41/Fe₃O₄ was measured by atomic absorption spectroscopy (AAS) technique that was found to be 1.89×10^{-10} ³ mol g⁻¹.

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The normal XRD and low angle XRD patterns of magnetic MCM-41 nanoparticles and Pd-imi-CC@MCM-41/Fe₃O₄ are shown in Figures 5 and 6. In normal

XRD patterns of magnetic MCM-41 nanoparticles, imi-CC@MCM-41/Fe₃O₄ and Pd-imi-CC@MCM-41/Fe₃O₄ (Figure 5) several peaks in 2 θ values of 30.7°, 35.6°, 43.3°,

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53.8°, 57.7° and 62.8° were observed, which were corresponded to crystal planes of Fe_3O_4 -doped into mesoporous channels of MCM-41. These results confirmed that the Fe_3O_4 -doped into mesoporous channels of MCM-41 did not lead to changes in the crystal phase of Fe_3O_4 . These results are in agreement with standard XRD pattern of Fe_3O_4 nanoparticles [47]. Also, a broad peak at 20-28° is related to silica skeleton. A good agreement was observed between normal XRD pattern of MCM-41/Fe_3O_4 with normal XRD patterns of imi-CC@MCM-41/Fe_3O_4 and Pd-imi-CC@MCM-41/Fe_3O_4 nanoparticles after modification.

Also, the peak positions of 2θ at 40.7° (200), 46.8° (220), and 67.5° (331) in normal XRD pattern of Pd-imi-CC@MCM-41/Fe₃O₄ are related to Pd(0) in the catalyst. These peaks are not presented in XRD patterns of MCM-41/Fe₃O₄ and imi-CC@MCM-41/Fe₃O₄. This result confirmed that Pd(0) successfully immobilized on MCM-41/Fe₃O₄ [28, 33].

Also, low angle XRD patterns of magnetic MCM-41 nanoparticles and Pd-imi-CC@MCM-41/Fe₃O₄ were performed, which are presented in Figure 6. The low angle XRD pattern of MCM-41/Fe₃O₄ shows the several peaks of 2θ value at $2\theta \approx 2.18^{\circ}$, $2\theta \approx 4.5^{\circ}$ and $2\theta \approx 5.5^{\circ}$ that is due to the hexagonal channel unit cell of MCM-41 [47, 48]. The mentioned peaks, appear in very low intensity due to immobilization of organic layers and palladium complex in MCM-41 channels [45, 47].





Figure 6. Low angle XRD patterns of magnetic MCM-41 nanoparticles (a) and Pd-imi-CC@MCM-41/Fe₃O₄ (b).

The thermogravimetric analysis was used to determine qualitative and quantitative analysis of organic groups, which were immobilized on the surface of MCM-41/Fe₃O₄. TGA/DTA analysis of Pd-imi-CC@MCM-41/Fe₃O₄ was performed using a heating rate of 15°C/min under an air atmosphere between room temperature to 700 °C.

TGA/DTA diagrams of Pd-imi-CC@MCM-41/Fe₃O₄ are shown in Figure 7, which shows the weight loss of the organic functional groups as it decomposes upon heating. The TGA curve of this catalyst shows the several steps of weight losses. The mass loss in low temperatures (25 %), is correspondence to the removal of organic solvents and water [49]. Second weight loss is 30 %, which was observed at 200-500 °C is due to calcination of organic moieties that was immobilized on MCM-41/Fe₃O₄ nanoparticles. Final weight loss is 5%, which was observed at high temperatures, may be related to thermal transformation of crystal phase of Fe₃O₄ nanoparticles and condensation of the silanol groups of MCM-41 [29, 47].

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Figure 7. TGA/DTA diagram of Pd-imi-CC@MCM-41/Fe₃O₄.

Nitrogen adsorption–desorption isotherms of mesoporous MCM-41/Fe₃O₄ and Pd-imi-CC@MCM-41/Fe₃O₄ are shown in Figure 8. Based on the IUPAC classification, the MCM-41/Fe₃O₄ material displayed an isotherm of type IV, which is according to mesoporous material [47, 50]. Based on Brunauer-Emmett-Teller (BET), the surface area of MCM-41/Fe₃O₄ and Pd-imi-CC@MCM-41/Fe₃O₄ are 911 and 8.5 m²/g, respectively. The BET surface area of Pd-imi-

CC@MCM-41/Fe₃O₄ is lower than MCM-41/Fe₃O₄ which is due to the grafting of organic layers and Pd-complex into channels of MCM-41 nanoparticles. The pore volume of MCM-41/Fe₃O₄ and Pd-imi-CC@MCM-41/Fe₃O₄ are 0.7 cm^3g^{-1} and 0.1 cm^3g^{-1} , respectively, and pore volume of catalyst is lower than MCM-41/Fe₃O₄, which is due to the grafting of organic layers and Pd-complex into channels of MCM-41 [47].

The FT-IR spectra for Fe₃O₄ nanoparticles, mesoporous MCM-41, MCM-41/Fe₃O₄, nPr-NH₂@MCM-41/Fe₃O₄, CC@MCM-41/Fe₃O₄, imi-CC@MCM-41/Fe₃O₄ and Pd-imi-CC@MCM-41/Fe₃O₄ are shown in Figure 9. The strong bands at 438 and 570 cm⁻¹ in the FT-IR spectrum of Fe₃O₄ nanoparticles (Figure 9, spectrum b) are related to the

vibrations of Fe-O bonds [17, 33], which these bands are present in FT-IR spectrum of MCM-41/Fe₃O₄ (Figure 9, spectrum c). The several peaks at 458, 810, and 1083 cm⁻¹ in FT-IR spectrum of mesoporous MCM-41 (Figure 9, spectrum a) are corresponded to the symmetric and asymmetric Si–O–Si vibrations in silica [29, 48], which these bands are present

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in FT-IR spectrum of MCM-41/Fe₃O₄. Also, a stretching vibrational mode at 951 cm⁻¹ in the FT-IR spectrum of MCM-41/Fe₃O₄ may be corresponded to the Fe-O-Si bonds from salinization of the magnetic nanoparticles [33, 45] which is not indicate in FT-IR spectra of MCM-41and Fe₃O₄ nanoparticles. All of these results are important witness for the successful preparation of MCM-41/Fe₃O₄.

The bands adsorption above 3000 cm⁻¹ are due to symmetrical and asymmetrical stretching vibrations of hydroxyl groups on the nanoparticles surface [44, 51]. Also,

the bending vibrational mode of the O-H bands on the surface of nanoparticles were indicated by a bandbat 1.630/16850em7k, which is due to the presence of an adsorbed water layer on the nanoparticles [33, 51].

Functionalization of MCM-41/Fe₃O₄ with APTES (Figure 9, spectrum d) was confirmed by C-H bands vibrations that is observed at 2930 cm⁻¹ [49, 52], which these peaks not indicate in FT-IR spectra **a-c**. The broad adsorption band at 1500-1630 cm⁻¹ in FT-IR spectra **e-g** may be related to the C=N and C=C bands, which overlapped with bending vibrational mode of the O-H bands.

Wavenumber cm-1

2.3 Catalytic activity of Pd-imi-CC@MCM-41/Fe $_3O_4$ in Suzuki and Heck reactions

Catalytic activity of Pd-imi-CC@MCM-41/Fe₃O₄ was studied in C-C coupling reactions such as Suzuki (Scheme 2) and Heck (Scheme 4) coupling reactions.

In order to obtain the best conditions for Suzuki coupling reaction, various parameters such as the amount of catalyst, solvent, base and temperature were examined in coupling reaction of iodobenzene with phenylboronic $(PhB(OH)_2)$ as model reaction. Results of these experiments were summarized in Table 1. Based on outlined results in Table 1, the best results were obtained in the presence of 8 mg (1.5

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mol%) of Pd-imi-CC@MCM-41/Fe₃O₄ in PEG-400 as green solvent using Na₂CO₃ (3 mmol) as base at 80 °C (Table 1, entry 3). When the model reaction was examined at 60 °C (Table 1, entry 14), the product yield was 48%. As shown in Table 1, model reaction did not proceed in the absence of Pdimi-CC@MCM-41/Fe₃O₄ (Table 1, entry 1). Meanwhile, the best results were obtained in the presence of $\sqrt{8}_{WW}$ mg_{le}(0,45 mol%) of Pd-imi-CC@MCM-41/Fe₃O₄ cast catalyst (Table24); entry 3) and lower amounts of Pd-imi-CC@MCM-41/Fe₃O₄ (5 mg) gave a lower yield (69%) of products (Table 1, entry 2).

Scheme 2. Carbon-Carbon coupling reaction of aryl halides with $PhB(OH)_2$ or 3,4-diF-PhB(OH)_2 in the presence of Pd-imi-CC@MCM-41/Fe₃O₄

Table 1. Optimization of Suzuki reaction conditions for coupling of iodobenzene with phenylboronic acid in the presence of Pd-imi-CC@MCM-41/Fe₃O₄.

Entry	Catalyst (mg)	Solvent	Base	Temperature (°C)	Time (min)	Yield (%) ^a
1	-	PEG	Na ₂ CO ₃	80	200	-
2	5	PEG	Na ₂ CO ₃	80	40	69
3	8	PEG	Na ₂ CO ₃	80	40	98
4	10	PEG	Na ₂ CO ₃	80	40	98
5	8	H_2O	Na ₂ CO ₃	80	60	64
6	8	EtOH	Na ₂ CO ₃	80	60	21
7	8	DMSO	Na ₂ CO ₃	80	40	97
8	8	DMF	Na ₂ CO ₃	80	35	98
9	8	Dioxane	Na ₂ CO ₃	80	60	77
10	8	PEG	Et ₃ N	80	60	56
11	8	PEG	NaOEt	80	60	30
12	8	PEG	NaOH	80	60	64
13	8	PEG	KOH	80	60	61
14	8	PEG	Na ₂ CO ₃	60	60	48
15	8	PEG	Na ₂ CO ₃	40	60	Trace

Catalytic activity of Pd-imi-CC@MCM-41/Fe₃O₄ was explored with differnt aryl halides and phenylboronic acid derivatives (Table 2). Aryl halides having electrondonating or electron-withdrawing groups on aromatic ring converted to biphenyl products in high yields and high TON and TOF values. High TOF and TON values were shows the highly efficiency of Pd-imi-CC@MCM-41/Fe₃O₄ in C-C coupling reactions as a hetereogeneous catalyst. As shown in Table 2, the coupling of phenylboronic acid with aryl iodide is faster than aryl bromide or aryl chloride. For example, the calculated TOF value for coupling of iodobenzene with PhB(OH)₂ is 98 h⁻¹ (Table 2, entry 1) that is higher than bromobenzene (35.2 h^{-1}) or chlorobenzene (2.5 h^{-1}) . Therefore, the reactivity of aryl halides are as: PhI>PhBr>PhCl. Also as shown in Table 2, aryl halydes with electron-withdrawing groups are more reactive than aryl halvdes bearning an electron-donating group. For example, the calculated TOF values for coupling of 4bromoanisole, 4-bromotoluene, bromobenzene, 4-Bromonitrobenzene and 4-Bromobenzonitrile with PhB(OH)₂ are 27.7, 42.2, 35.2, 65.3 and 86 h⁻¹, respectively. Based on these data, the reactivity of parafunctionalized bromobenzenes can be sorted as: 4-CN>4-NO₂>H>4-Me>4-OMe. Also, the calculated TOF value for coupling of 3-bromoanisole with PhB(OH)₂ is 30.3 h⁻ ¹ (Table 2, entry 19), which is higher than 4-bromoanisole $(27.7 h^{-1})$, because electron-withdrawing effect of parafanctional groups are hgiher than metafunctional groups.

In order to extend the scope of this procedure, the coupling of various aryl halides with 3,4diflorophenylboronic acid (Table 2, entries 21-28) were investigated. As expected, aryl iodides exhibit more reactivity than aryl bromides. As shown in Table 2, high catalytic activity of Pd-imi-CC@MCM-41/Fe₃O₄ and high TON and TOF values of obtained products were observed in carbon-carbon coupling reactions.

The selectivity of this catalytic system was investigated for the coupling of 1-bromo-4-chorobenzene with phenylboronic acid (Table 2, entry 2) and 3,4-

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diflorophenylboronic acid (Table 2, entry 27). As shown in Scheme 3, chloro functional group was not coupled with phenylboronic acid derivatives, and coupling of bromo functional group was observed. Also the coupling of 4-bromophenol with phenylboronic acid (Table 2, entries 17 and 18) was examined in the presence of this catalyst, which C-O coupling was not observed and pure biphenyl from Suzuki reaction was obtained in good yield. Therefore, this procedure is efficient and capable for wide range of various aryl halides.

Table 2. Catalytic C-C coupling reaction of aryl halides using phenylboronic acid and 3,4-diflorophenylboronic acid
in the presence of Pd-imi-CC@MCM-41/Fe ₃ O ₄ .

Entry	Aryl halide	phenylating reagent	Time (min)	Yield (%) ^a	TON	TOF (h-1)	Melting point (°C)	Reported M.P. [Ref.]
1	I	PhB(OH) ₂	40	98	65.3	98.0	65-68	66-68 [52]
2	Cl Br	PhB(OH) ₂	50	95	63.3	76.0	69-72	71-73 [17]
3	Me	PhB(OH) ₂	90	95	63.3	42.2	45-46	45-47 [29]
4	MeO	PhB(OH) ₂	80	92	61.3	46.0	80-82	82-84 [29]
5	NC	PhB(OH) ₂	45	97	64.7	86.2	81-83	80-84 [29]
6	I Me	PhB(OH) ₂	220	92	61.3	16.7	Oil	Oil [33]
7	O ₂ N Br	PhB(OH) ₂	55	98	65.3	71.3	111-114	113-115 [53]
8	Me	PhB(OH) ₂	45	96	64.0	85.3	44-47	45-47 [29]
9	MeO	PhB(OH) ₂	130	90	60.0	27.7	81-83	82-84 [29]
10	Br	PhB(OH) ₂	100	88	58.7	35.2	65-68	66-68 [52]
11	Cl	PhB(OH) ₂	24 h	89	59.3	2.5	65-68	66-68 [52]
12	NC	PhB(OH) ₂	210	95	63.3	18.1	80-83	80-84 [29]

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13	OHC	PhB(OH) ₂	90	88	58.7	39.1	54-56	View Article Online 55-57 [33]
14	OHC Br	PhB(OH) ₂	110	90	60.0	32.7	Oil	Oil [53]
15	O ₂ N Cl	PhB(OH) ₂	260	90	60.0	13.8	111-115	113-115 [53]
16	HO	PhB(OH) ₂	24 h	85	56.7	2.4	160-163	162-164 [28]
17	HOBR	PhB(OH) ₂	120	89	59.3	29.7	159-163	162-164 [28]
18	MeO	PhB(OH) ₂	120	91	60.7	30.3	Oil	Oil [53]
19	I	3,4-diF- PhB(OH) ₂	50	97	64.7	77.6	39-41	39-41 [52]
20	Br	3,4-diF- PhB(OH) ₂	120	90	60.0	30.0	39-41	39-41 [52]
21	Me	3,4-diF- PhB(OH) ₂	75	96	64.0	51.2	42-43	-
22	NC	3,4-diF- PhB(OH) ₂	90	97	64.7	43.1	104-106	-
23	H ₃ CO	3,4-diF- PhB(OH) ₂	100	92	61.3	36.8	Oil	-
24	H ₃ CO Br	3,4-diF- PhB(OH) ₂	125	86	57.3	27.5	Oil	-
25	Cl	3,4-diF- PhB(OH) ₂	70	87	58.0	49.7	59-60	-
26	O ₂ N Br	3,4-diF- PhB(OH) ₂	70	97	64.7	55.4	117-120	119-120 [52]
^a Isolated vield.								

Also, catalytic activity of Pd-imi-CC@MCM-41/Fe₃O₄ has been studied in Heck cross coupling reaction, which is outlined in Scheme 4. In order to found the best reaction conditions, the coupling of iodobenzene with butyl acrylate was selected as model reaction. Effect of various parameters (such as solvent, temperature, amount of catalyst, and nature of base) were studied in model reaction and the results of these studies are summarized in Table 3. The coupling of iodobenzene with butyl acrylate has been examined in the presence of different amount of Pd-imi-CC@MCM-41/Fe₃O₄ and the best results (including yield of product and time reaction) were obtained in the present of 0.012 g (contaning 2.27 mol% of palladium) of catalyst (Table 3, entry 4). As shown in Table 3, the model reaction was not proceeded in the absent of catalyst (Table 3, entry 1) and also low yield of product was observed in the precent of lower amounts of catalyst (Table 3, entries 2 and 3). Among the various solvents (Table 3, entries 5-9) and bases (Table 3, entries 9-13), the best results were observed in PEG-400 as solvent and sodium carbonate as base. In the temperature effect study (Table 3, entries 13 and 14), the best results were obtained at 120 °C.

Scheme 4. Heck coupling reaction in the presence of Pd-imi-CC@MCM-41/Fe₃O₄.

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Table 3 with bu	3. Optimiz	ation con	ditions for esence of	or the coupling Pd-imi-CC@M	of iodo ICM-41/	benzene Fe ₃ O ₄ .	8 9	12 12	Dioxane DMF	NaCO ₃ NaCO ₃	120 120	100 80	18 97
Entw	Catalyst	Salvant	Daga	Temperature	Time	Yield	10	12	PEG	KOH	120	100	40
Entry	(mg)	Solvent	Base	(°C)	(min)	(%) ^a	11	12	PEG	Et ₃ N	120	100	80
1	-	PEG	NaCO ₃	120	600	-	12	12	PEG	NaOEt	120	100	59
2	5	PEG	NaCO ₃	120	80	51	13	12	PEG	NaOH	120	100	47
3	10	PEG	NaCO ₃	120	80	68	14	12	PEG	NaCO ₃	100	80	61
4	12	PEG	NaCO3	120	80	96	^a Isolate	d vield.					

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The scope of this procedure was extended for the coupling of various aryl halides with butyl acrylate in the presence of Pd-imi-CC@MCM-41/Fe₃O₄ (Table 4). All aryl halides (including electron-donating and electron-withdrawing functional groups on aromatic ring) were converted to corresponding products with good yields and high TON and TOF values. As shown in Table 4, the coupling of para-functionalized aryl halides is faster than ortho-functionalized aryl halides. For example, the calculated TOF values for coupling of 4-iodotoluene and 2-iodotoluene with butyl acrylate are 25.9 and 11.8 h⁻¹,

respectively. Based on these data, the reactivity of parafunctionalized aryl halides are higher 10tham Northow functionalized aryl halides due to steric hindrance of ortho-functional groups.

In order to extend the scope of this procedure, the coupling of aryl halides with methyl acrylate (Table 4, entries 6-10) and acrylonitrile (Table 4, entries 11-15) were investigated and all products were obtaind in good yields with high TON and TOF values.

Table 4. Coupling of aryl halides with butyl acrylate, methyl acrylate and acrylonitrile in the presence of Pd-imi-
 $CC@MCM-41/Fe_3O_4$.

Entry	Aryl halide	Alkene	Time (min)	Yield (%)ª	TON	TOF (h ⁻¹)	Melting point (°C)	Reported melting point (°C)
1	I	Butyl acrylate	80	96	42.3	31.7	Oil	Oil [48]
2	I	Butyl acrylate	200	89	39.2	11.8	Oil	Oil [54]
3	OMe	Butyl acrylate	220	95	41.8	11.4	Oil	Oil [33]
4	MeO	Butyl acrylate	110	96	42.3	23.1	Oil	Oil [29]
5	Me	Butyl acrylate	100	98	43.2	25.9	Oil	Oil [17]
6	I	Methyl acrylate	65	94	41.4	38.2	28-30	Oil [55]
7	Me	Methyl acrylate	75	97	42.7	34.2	54-56	55-57 [56]
8	U OMe	Methyl acrylate	180	87	38.3	12.8	Oil	Oil [57]
9	Me	Methyl acrylate	160	91	40.1	15.0	Oil	[58]
10	MeO	Methyl acrylate	90	93	41.0	27.3	86-88	88-91 [56]
11	I	Acrylonitrile	100	93	40.1	24.6	Oil	Oil [54]
12	MeO	Acrylonitrile	145	90	39.6	16.4	Oil	Oil [59]

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^a Isolated yield.

2.4 Reusability of the Catalyst

The recoverability of Pd-imiand reusability CC@MCM-41/Fe₃O₄ was examined in the coupling of iodobenzene with PhB(OH)2. The obtained results from reusing of this catalyst were summarized in Figure 10. For this aim, in the end of the each reaction run, the catalyst was recovered by an external magnet and washed with ethyl acetate to obtain the product. The recovered catalyst was reused for next run. As shown in Figure 10, this catalyst can be reused up to 8 times without significant loss in its catalytic activity or any increase in reaction time. TON value for 8 times reusing of this catalyst is 520. Also, the average isolated yields is 97.5%.

Figure 10. Recyclability of Pd-imi-CC@MCM-41/Fe₃O₄ in the coupling of iodobenzene with PhB(OH)2.

2.5 characterization of recovered catalyst

of Pd-imi-In order to show the structure stability CC@MCM-41/Fe₃O₄ after recycling, separated catalyst was characterized by SEM, FT-IR and AAS techniques. The particle size and morphology of catalyst after recycling studied by SEM technique. The SEM images of recovered catalyst was shown in Figure 11. As it can be seen, the morphology and size of catalyst after recycling is as same as fresh catalyst. These results indicate that the size and morphology of catalyst doesn't changed after recycling.

Figure 11. SEM images of recycled Pd-imi-CC@MCM-41/Fe₃O₄.

the recovered Pd-imi-CC@MCM-41/Fe₃O₄ was Also. characterized by FT-IR technique and compared to fresh catalyst. FT-IR spectra of recovered catalyst and fresh catalyst are shown in Figure 12, which there is no any change in FT-IR of recovered catalyst compared with fresh one. These results are strong evidence for stability of Pd-imi-CC@MCM-41/Fe₃O₄ after recycling, therefore this catalyst can be recovered and recycled without any change in its structure.

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2.6 Poisoning test

Poisoning test was commonly used for homogeneity/heterogeneity nature of catalysis procedures, which was often performed using PVP or mercury [60-62].

As shown in Scheme 1, palladium is immobilized on modified MCM-41/Fe₃O₄ structure by covalent bond. If little amount of the palladium leached into reaction solution during C-C coupling reaction, both heterogeneous (supported) and homogeneous (leached) palladium play as catalyst in the reaction. However, if insoluble ligand (which can coordinate with palladium) is added in the reaction mixture, the catalytic activity of homogeneous (leached) palladium will be stopped. Pyridines are known ligands, which easily coordinated with palladium [63]. Therefore, herein commercially available PVP was selected for the poisoning test study. In order to consider homogeneity/heterogeneity nature of Pd-imi-CC@MCM-41/Fe₃O₄, the Suzuki coupling reaction of iodobenzene (1 mmol) with phenylboronic acid (1 mmol) in the

presence of PVP (8 mg) and Pd-imi-CC@MCM_41/Fe₂O₄₁/Fe₃O₄ mg, 1.5 mol%) was performed undep_optimized on the condition (in PEG as solvent, sodium carbonate as base at 80 °C). In this study, any change was not observed in the conversion of starting materials to products and reaction was completed after 40 min, which suggests that Pd-imi-CC@MCM-41/Fe₃O₄ is heterogeneous in nature. Therefore, during the C-C coupling reaction, the palladium doesn't leached into reaction solution and heterogeneous (supported) palladium is as only catalyst in described reaction.

2.7 Leaching Study of the catalyst

In order to explore the heterogeneous nature of Pd-imi-CC@MCM-41/Fe₃O₄, leaching study of this catalyst was performed. In this regard, coupling of iodobenzene with phenylboronic acid was selected as model reaction. In order to determine the palladium concentration in reaction solution, catalyst was removed after 40 min without cooling and further the remained reaction solution was analyzed by AAS. In this analysis, the palladium concentration in solution was very small, which found to be 0.000056 mmol mL⁻¹. It could be found that a very small amount of palladium in reaction solution did not have a significant effect on the reaction progress. Therefore completion of the reaction could be attributed to the heterogeneous palladium species. These results proves that Pd-imi-CC@MCM-41/Fe₃O₄ has heterogeneous nature.

2.8 Comparison of the Catalyst

The efficiency of Pd-imi-CC@MCM-41/Fe₃O₄ was studied by comparing of obtained results from previously reported catalysts with this catalyst for the coupling of 4-iodotoluene with phenylboronic acid. Results of this comparison are summarized in Table 5. As shown, in the presence of Pd-imi-CC@MCM-41/Fe₃O₄ as catalyst, the reaction yield is higher and reaction time is lower than previously reported catalysts. Also, the higher TON and TOF values was observed in the presence of Pd-imi-CC@MCM-41/Fe₃O₄ than other catalysts. Also, several previously reported procedures were applied microwave irradiation (Table 5, entries 11 and 12) or ultrasonic sonication (Table 5, entry 12) to perform Suzuki coupling reaction.

Table 5. Comparison of Pd-imi-CC@MCM-41/Fe $_{3}O_{4}$ in the coupling of 4-Iodotoluene with phenylboronic acid with previously reported procedures.

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Entry	Catalyst	Reaction conditions	Time	TON	TOF	Yield ^a (%)
	, ,		(min)		(h-1)	[Reference]
1	Pd(0)-ABA-Fe ₃ O ₄	H ₂ O, Et ₃ N, 80 °C	180	171	57	96 [17]
2	Pd-Arg-boehmite	PEG-400, Na ₂ CO ₃ , 80 °C	240	84	21.1	91 [38]
3	Pd(0)–SMTU–boehmite	H ₂ O, Na ₂ CO ₃ , 80 °C	90	108	72	87 [51]
4	N,N'-bis(2-pyridinecarboxamide)-1,2- benzene palladium complex	H ₂ O, K ₂ CO ₃ , 100 °C	240	93	23	93 [64]
5	Pd/Au NPs	EtOH/H ₂ O, K ₂ CO ₃ , 80 °C	24h	21	0.89	86 [65]
6	Pd NP	H ₂ O, KOH, 100 °C	12h	94	7.8	94 [66]
7	CA/Pd(0)	H ₂ O, K ₂ CO ₃ , 100 °C	180	190	63	95 [67]
8	Polymer anchored Pd(II) Schiff base complex	K ₂ CO ₃ , DMF: H ₂ O (1:1), 80 °C	480	182	22	91 [68]
9	Pd@SBA-15/ILDABCO	K ₂ CO ₃ , H ₂ O, 80 °C	120	194	97	97 [69]
10	SBA-16-2 N-Pd(II)	EtOH, K ₂ CO ₃ , 60 °C	120	194	97	97 [70]
11	Pd nanocatalyst	solvent-free, K ₂ CO ₃ , MW (400 W), 50 °C	5	18	225	72 [71]
12	Pd NPs@CMC/AG	H ₂ O, K ₂ CO ₃ , MW, 60 °C, ultrasonic sonication	30	75	150	75 [72]

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1	n	11	114	n	a	Ε.		a	m	ρ
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13	CNT-Fe3O4@(A-V)-silica-Pd	EtOH, Cs ₂ CO ₃ , reflux conditions	480	62	7.75 93 73 v Article Online DOI: 10.10397C9NJ027271
14	Pd-imi-CC@MCM-41/Fe ₃ O ₄	PEG-400, Na ₂ CO ₃ , 80 °C	45	65.3	98.0 96 [this work]

3 Experimental

3.1. Preparation of the catalyst

In the first step, amino-functionalized magnetic MCM-41 prepared nanoparticles $(nPr-NH_2@MCM-41/Fe_3O_4)$ according to new reported procedure [44]. In the next step, 1 g of nPr-NH₂@MCM-41/Fe₃O₄ was dispersed in toluene and mixed with 2.5 mmol of cyanuric chloride (CC). Then, this mixture was stirred under reflux conditions for 24 h. The resulting solid (CC@MCM-41/Fe₃O₄) was separated using assistance of external magnet, washed with ethanol and dried at room temperature. Then, CC@MCM-41/Fe₃O₄ (1g) was dispersed in 50 mL toluene by sonication for 20 min, and 1methylimidazole (5 mmol) was added to the reaction mixture. The reaction mixture was stirred under reflux conditions for 24 h under N₂ atmosphere. The resulting nanoparticles (imi-CC@MCM-41/Fe₃O₄) were washed with ethanol for several times and separated via magnetic decantation and dried at 50 °C. In the final step, 0.5 g of imi-CC@MCM-41/Fe₃O₄ and 0.25 g of palladium acetate were dispersed in DMSO for 20 min and stirred under N₂ atmosphere at room temperature for 3 h and was allowed to continue for 12 h at 60 °C. The reaction mixture was allowed to continue for 4 h at 100 °C. final product (Pd-imi-CC@MCM-41/Fe₃O₄) was The separated by magnetic decantation and washed by ethanol and water to remove the unattached substrates and dried at room temperature.

3.2 General procedure for Suzuki reaction catalyzed by Pd-imi-CC@MCM-41/Fe₃O₄

A mixture of aryl halide (1 mmol), 1 mmol of phenylboronic acid (PhB(OH)₂) or 3,4-difluoro phenylboronic acid (3,4-diF-PhB(OH)₂), Na₂CO₃ (3 mmol, 0.318 g), and Pd-imi-CC@MCM-41/Fe₃O₄ (0.008 g, 1.5 mol%) was stirred in PEG-400 (1 mL) at 80 °C and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled down, Pd-imi-CC@MCM-41/Fe₃O₄ was separated using an external magnet and washed with ethyl acetate. The remaining reaction mixture was dried over anhydrous Na₂SO₄ (1.5 g). Then ethyl acetate was evaporated and pure biphenyl derivatives were obtained in 85 to 98% of yields.

3.3 General procedure for Heck reaction catalyzed by Pdimi-CC@MCM-41/Fe₃O₄

A mixture of aryl halide (1 mmol), 1.2 mmol of alkene (butyl acrylate, methyl acrylate or acrylonitrile), Na₂CO₃ (3 mmol, 0.318 g), and Pd-imi-CC@MCM-41/Fe₃O₄ (0.012 g, 2.27 mol%) was stirred in PEG-400 (1 mL) at 120 °C and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled down to room temperature, Pd-imi-CC@MCM-41/Fe₃O₄ was separated using an external magnet and washed with diethyl ether. Then, the reaction mixture was extracted with H₂O and diethyl ether. The organic layer was dried over anhydrous Na₂SO₄ (1.5 g). The diethyl ether was evaporated and pure products were obtained in 88 to 98% of yields.

3.4. Selected spectral data

3,4-Difluoro-4'-nitro-1,1'-biphenyl: ¹H NMR (400 MHz, CDCl₃): δ_{H} = 8.36-8.32 (dt, *J*= 8.8 Hz, *J*= 2 Hz, 2H), 7.73-7.70 (dt, *J*= 8.8 Hz, *J*= 2 Hz, 2H), 7.50-7.45 (m, 1H), 7.41-7.37 (m,1H), 7.36-7.31 (m,1H), ppm; ¹³C NMR (100 MHz, CDCl₃): δ_{H} = 152.2, 152.1, 152.0, 151.9, 149.7, 149.6, 149.5, 149.4, 147.4, 145.4, 135.9, 135.84, 135.82, 135.7, 127.7, 124.3, 123.63, 123.60, 123.57, 123.54, 118.2, 118.0, 116.6, 116.4 ppm; ¹⁹F NMR (400 MHz, CDCl₃): δ_{H} = -136.2 (d, 1F), -137.1 (d, 1F)ppm.

3,4-Difluoro-3'-methoxy-1,1'-biphenyl: ¹H NMR (400 MHz, CDCl₃): δ_{H} = 7.44-7.38 (dd, *J*= 8 Hz, *J*= 4 Hz, 2H), 7.35-7.32 (m, 1H), 7.29-7.24 (m, 1H), 7.16-7.13 (d, *J*= 12Hz, 1H), 7.10 (s, 1H), 6.97-6.95 (d, *J*= 8 Hz, 1H), 3.91 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.0, 151.8, 151.3, 151.2, 149.3, 148.8, 148.7, 140.6, 138.2, 130.0, 123.1, 123.0, 119.4, 117.6, 117.4, 116.2, 116.0, 113.1, 112.8, 55.3 ppm; ¹⁹F NMR (400 MHz, CDCl₃): δ_{H} = -137.7 (d, 1F), -140.2 (d, 1F)ppm.

[1,1'-Biphenyl]-3-carbaldehyde: ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ = 10.14 (s, 1H), 8.42 (s, 1H), 8.17-8.15 (d, *J*= 8Hz, 1H), 7.9-7.88 (t, *J*= 8Hz, 1H), 7.70-7.66 (m, 2H), 7.63-7.58 (q, *J*= 8 Hz, 1H), 7.54-7.50 (t, *J*= 8 Hz, 2H), 7.46-7.42 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 192.5, 141.6, 139.9, 132.5, 129.9, 129.0, 129.0, 128.9, 128.0, 127.9, 127.2 ppm.

3-Methoxy-1,1'-biphenyl: ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ = 7.64-7.62 (d, *J*= 8Hz, 2H), 7.49-7.45 (t, *J*= 8 Hz, 2H), 7.42-7.37 (six, *J*= 4 Hz, 2H), 7.23-7.21 (d, *J*= 8 Hz, 1H), 7.17-7.15 (t, *J*= 4 Hz, 1H), 6.95-6.92 (dd, *J*= 8 Hz, *J*= 4 Hz, 1H), 3.91 (s, 3H) ppm.

2-Methyl-1,1'-biphenyl: ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ = 7.51-7.47 (t, *J*= 8Hz, 3H), 7.44-7.40 (t, *J*= 8 Hz, 3H), 7.35-7.32 (m,3H), 2.36 (s, 3H) ppm.

3',4'-Difluoro-[1,1'-biphenyl]-4-carbonitrile: ¹H NMR (400 MHz, CDCl₃): δ_{H} = 7.78-7.76 (d, *J*= 8Hz, 2H), 7.67-7.65 (d, *J*= 8 Hz, 2H), 7.46-7.41 (m,1H), 7.38-7.34 (m,1H), 7.32-7.28 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 151.9, 149.6, 143.5, 136.2, 132.8, 127.6, 123.4, 123.4, 123.4, 123.3, 118.7, 118.2, 118.0, 116.4, 116.2, 111.6 ppm; ¹⁹F NMR (400 MHz, CDCl₃): δ_{H} = -136.4 (d, 1F), -137.6 (d, 1F)ppm.

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Butyl cinnamate: ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ = 7.74-7.70 (d, *J*= 16 Hz, 1H), 7.57-7.55 (m, 2H), 7.42-7.40 (t, *J*= 4 Hz, 3H), 6.50-6.46 (d, *J*= 16 Hz, 1H), 4.27-4.23 (t, *J*= 8 Hz, 2H), 1.77-1.69 (quint, *J*= 8 Hz, 2H), 1.52-1.43 (sextet, *J*= 8 Hz, 2H), 1.02-0.98 (t, *J*= 8 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ =167.1, 144.6, 134.5, 130.2, 128.9, 128.1, 118.3, 64.4, 30.8, 19.2, 13.8 ppm.

Butyl 3-(4-methylphenyl)acrylate: ¹H NMR (400 MHz, CDCl₃): δ_{H} = 7.72-7.68 (d, *J*= 16 Hz, 1H), 7.48-7.45 (d, *J*= 12 Hz, 2H), 7.23-7.21 (d, *J*= 8 Hz, 2H), 6.45-6.41 (d, *J*= 16 Hz, 1H), 4.26-4.22 (t, *J*= 8 Hz, 2H), 2.40 (s, 3H), 1.76-1.69 (quint, *J*= 8 Hz, 2H), 1.52-1.43 (sextet, *J*= 8 Hz, 2H), 1.02-0.98 (t, *J*= 8 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ =167.3, 144.6, 140.6, 131.7, 129.6, 128.1, 117.2, 64.4, 30.8, 21.5, 19.3, 13.8 ppm.

Butyl 3-(2-methylphenyl)acrylate: ¹H NMR (400 MHz, CDCl₃): δ_{H} = 78.03-7.99 (d, *J*= 16 Hz, 1H), 7.60-7.58 (d, *J*= 8 Hz, 1H), 7.31-7.30 (d, *J*= 4 Hz, 1H), 7.26-7.2 (t, *J*= 8 Hz, 2H), 6.42-6.38 (d, *J*= 16 Hz, 1H), 4.27-4.23 (t, *J*= 8 Hz, 2H), 2.48 (s, 3H), 1.77-1.70 (quint, *J*= 8 Hz, 2H), 1.53-1.43 (sextet, *J*= 8 Hz, 2H), 1.02-0.98 (t, *J*= 8 Hz, 3H) ppm.

3-(o-Tolyl)acrylonitrile: ¹H NMR (400 MHz, CDCl₃): δ_{H} = 7.75-7.71 (d, *J*= 16 Hz, 1H), 7.50-7.49 (d, *J*= 4 Hz, 1H), 7.38-7.34 (d, *J*= 8 Hz, 1H), 7.33-7.29 (m, 1H), 7.27-7.25 (d, *J*= 8 Hz, 1H), 5.86-5.82 (d, *J*= 16 Hz, 1H), 2.44 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ =148.5, 132.6, 131.1, 131.0, 130.6, 126.6, 125.6, 118.4, 97.2, 19.6 ppm.

3-(p-Tolyl)acrylonitrile: ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ = 7.42-7.38 (d, *J*= 16 Hz, 1H), 7.37-7.36 (d, *J*= 4 Hz, 2H), 7.26-7.24 (d, *J*= 8 Hz, 2H), 5.87-5.83 (d, *J*= 16 Hz, 1H), 2.42 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ =150.5, 141.9, 130.9, 129.8, 127.4, 118.5, 95.1, 21.5 ppm.

Cinnamonitrile: ¹H NMR (400 MHz, CDCl₃): δ_{H} = 7.53-7.41 (m, 6H), 5.94-5.90 (d, *J*= 16 Hz, 1H) ppm.

Methyl 3-(o-tolyl)acrylate: ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ = 8.04-8.00 (d, *J*= 16 Hz, 1H), 7.59-7.57 (d, *J*= 8 Hz, 1H), 7.33-7.29 (t, *J*= 8 Hz, 1H), 7.26-7.23 (t, *J*= 8 Hz, 2H), 6.42-6.38 (d, *J*= 16 Hz, 1H), 3.85 (s, 3H), 2.48 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ =167.5, 142.5, 137.7, 133.4, 130.8, 130.0, 126.4, 126.3, 118.8, 51.7, 19.8 ppm.

Methyl cinnamate: ¹H NMR (400 MHz, CDCl₃): $\delta_{\rm H}$ = 7.75-7.71 (d, *J*= 16 Hz, 1H), 7.57-7.54 (m, 2H), 7.43-7.41 (m, 3H), 6.50-6.46 (d, *J*= 16 Hz, 1H), 3.84 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ =167.4, 144.9, 134.4, 130.3, 128.9, 128.1, 117.8, 51.7 ppm.

4 Conclusions

In conclusion, an efficient and reusable heterogeneous catalyst (Pd-imi-CC@MCM-41/Fe_{3}O_{4}) was synthesized and

successfully applied for the selective C-C bond forming reactions. All products were obtained in the high of turnover numbers (TON) and turnover frequency (TOF), which is confirmed the high efficiency of this catalyst. Pd-imi-CC@MCM-41/Fe₃O₄ is composed from mesoporous MCM-41 and Fe₃O₄ magnetic nanoparticles, therefore it has advantages of both mesoporous materials (such as high surface area) and magnetic nanoparticles (such as fast and easy separation using an external magnet). Heterogeneity nature of Pd-imi-CC@MCM-41/Fe₃O₄ was studied by poisoning test and AAS technique.

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reactions

Bahman Tahmasbi*, Arash Ghorbani-Choghamarani

Nanoboehmite was prepared in water using commercially materials. Then palladium has been immobilized on its surface and applied as reusable organometallic nanocatalyst for C-C coupling reactions. The pure products were obtained in high yields, excellent TON and TOF numbers which were indicate the high efficiency of this catalyst. Selectivity of this catalyst was studied in various aryl halides which are bearing different functional groups. Heterogeneity and stability of this catalyst was studied by AAS technique, leaching test, poisoning test and characterization of recovered catalyst.

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