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# **Pd-** Dithizone grafted onto magnetic nanoparticles and study of its catalyticactivity in C-C and C-N coupling reactions

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Funding information Ilam University In this paper, we report a simple, facile and efficient method for the synthesis of  $Fe_3O_4/SiO_2$ -DTZ-Pd. The immobilized palladium was an efficient catalyst without addition of phosphine ligands for Stille, Heck and N-arylation reactions. This method has some advantages such as high yields and easy work up of products. In addition, the catalyst can be recovered using a magnet and reused several times without significant loss of its catalytic activity. This catalyst was characterized by various physico-chemical techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and inductively coupled plasma (ICP).

#### **KEYWORDS**

amination, dithizone, Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd, Heck reactions, heterogeneous catalysis, stille reaction

## **1 | INTRODUCTION**

An intriguing aspect of modern chemical research is catalytic reactions that has important strategy in fundamental research and industrial applications and play an important role in the synthesis of fine chemicals and advanced functional materials.<sup>[1,2]</sup> Generally, catalysts are divided into two groups: Most are homogeneous and the others are heterogeneous systems.<sup>[3]</sup> Despite beneficial effects with a homogeneous catalyst, it has significant drawbacks including low catalyst stability, difficulties in recovery and regeneration, possible toxicity caused by residual metal species, deactivation of the catalyst and high cost of the catalyst.<sup>[4,5]</sup> Therefore, the heterogenization of homogeneous catalysts can help in their use for practical processes to overcome the problems mentioned above.<sup>[6]</sup> In the same context, metal complexes have been immobilized on various supports such as mesoporous silica, alumina, zeolites, organic polymers and magnetic nanoparticles.[7-10]

In the recent decades, magnetic nanoparticles are attractive candidates as heterogeneous catalysts owing stability, high surface area, high activity and their magnetic properties that easily separated from the reaction media with an external magnet.<sup>[11]</sup> Furthermore, magnetic nanoparticles are useful for biomedical applications and industrial applications that covered a broad spectrum such as magnetic seals in motors, magnetic inks for bank cheques.<sup>[12]</sup>

The chemistry of organopalladium has made notable progress over the last 30 years. That progress is still continuing without any end. Carbon–carbon and carbon–heteroatom couplings are most important reactions in organic synthesis<sup>[13]</sup> due to they formed new bonds with carbon under extremely mild conditions. Most of these cross-coupling reactions have been reported to be promoted by Pd salts and complexes. Palladium catalyzed cross-coupling reactions being widely applied for the synthesis of fine chemicals, functional materials, industrial starting materials, pharmaceuticals and biologically active compounds.<sup>[14]</sup>

Herein we report the synthesis and characterization of a palladium complex immobilized on  $Fe_3O_4$  ( $Fe_3O_4/SiO_2$ -dtz-Pd), which exhibits a high catalytic activity in the Heck and Stille cross-coupling reactions and synthesis of anilines from aryl halides.

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## **2** | EXPERIMENTAL SECTION

### 2.1 | Materials

The reagents and solvents used in this work were all purchased from Sigma-Aldrich, Fluka or Merck Chemical Companies and utilized without further purification. Powder XRD was collected with a Rigaku-Dmax 2500 diffractometer with nickel filtered Cu K $\alpha$  radiation ( $\lambda = 1.5418$  °A, 40 kV). The particle morphology was examined using SEM with an FESEMTESCAN MIRA3. TEM of the NPs were recorded using a Zeiss-EM10C TEM. Supermagnetic properties of catalyst was measured on Vibrating Sample Magnetometer (VSM) MDKFD operating at room temperature.

## 2.2 | Preparation of Fe<sub>3</sub>O<sub>4</sub> MNPs

Bare Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles were prepared according to our recently reported work *via* chemical coprecipitation method using FeCl<sub>3</sub>  $6H_2O$  and FeCl<sub>2</sub>  $6H_2O$  in basic solution at 80 °C.<sup>[15]</sup>

# **2.3** | Preparation of Fe<sub>3</sub>O<sub>4</sub>-(3-chloropropyl) triethoxysilane (CPTES)

The obtained magnetic nanoparticles (MNPs) powder (1.5 g) was dispersed in a mixture of EtOH and water (25 ml, 1:1 by volume) by sonication for 30 min. Then 3-chloropropyl triethoxysilane (95%, 3 ml) was added to the mixture and stirred at room temperature under nitrogen atmosphere for 8 h. Then product was washed with deionized water and EtOH and magnetically decanted and dried at room temperature overnight.

## 2.4 | Preparation of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ

Chloro-functionalized MNPs (1.0 g) and dithizone (3.0 mmol) were dispersed in DMF (10 ml) by sonication for 10 min. The reaction mixture was stirrer for 30 h at 100 °C. The product was isolated using an external magnet, washed thoroughly with DMF and dried under vacuum for 12 h.

### 2.5 | Preparation of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd.

 $Fe_3O_4/SiO_2$ -DTZ (0.5 g), was added to a round-bottom flask containing EtOH (20 ml) and Pd (OAc)<sub>2</sub> (0.25 mmol). The mixture was stirred vigorously under reflux for 20 h. Then, NaBH<sub>4</sub> (0.3 mmol) was added to the reaction mixture and reaction was continued for another 2 h. The resulting solid was isolated using a magnetic field. The corresponding modified magnetic nanoparticles were thoroughly washed with EtOH and dried under vacuum at room temperature.

# **2.6** | General procedure for C–C coupling reaction using aryl halides and triphenyltin chloride (Stille reaction)

The catalytic activity of the synthesized  $Fe_3O_{4/}SiO_2$ -DTZ-Pd nanocatalyst was investigated with the Stille reaction that was carried out as follow: a mixture of aryl halide (1.0 mmol), triphenyltin chloride (0.5 mmol), Na<sub>2</sub>CO<sub>3</sub> (3.0 mmol) and  $Fe_3O_4/SiO_2$ -DTZ-Pd (0.005 g) was added to PEG (2.0 ml) as solvent. The reaction mixture was stirred at 80 °C and the progress of the reaction, the catalyst was separated using an external magnet and washed with diethyl ether and reused for the next experiment; the mixture was diluted with diethylether and water. The organic layer was separated, then the solvent was evaporated and pure biphenyl derivatives were obtained in good to excellent yields.

## 2.7 | General procedure for C–C coupling reaction using aryl halides with butyl acrylate (Heck reaction)

A mixture of aryl halide (1.0 mmol), butyl acrylate (1.2 mmol),  $K_2CO_3$  (3.0 mmol) and  $Fe_3O_4/SiO_2$ -DTZ-Pd (0.007 g) was added to PEG (2.0 ml) as a solvent. The reaction mixture was stirred at 100 °C and the progress of the reaction was monitored using TLC. After completion of the reaction, the mixture was cooled to room temperature and the catalyst was separated using an external magnet and washed with diethyl ether. The reaction mixture was extracted with water and diethyl ether. The organic layer was separated, and the solvent was evaporated and pure products were obtained in good to excellent yields.

# **2.8** | General procedure for N-arylationusing aryl halides with aqueous ammonia

A mixture of aryl halide (1 mmol), aqueous ammonia (28%) (2 ml) and 0.005 g of  $Fe_3O_4/SiO_2$ -DTZ-Pd was added to a round-bottom flask in neat conditions The reaction mixture was stirred at 60 °C and the progress of the reaction was monitored using TLC. After completion of the reaction, the catalyst was separated using an external magnet and the product was extracted by water and ethyl acetate. The organic layer was separated and the solvent was evaporated and pure products were obtained.

### 2.9 | Results and discussion

The MNPs/SiO<sub>2</sub>-DTZ-Pd complex was synthesized by several steps, which was shown in Scheme 1. First, MNPs was reacted with 3-(chloropropyl) triethoxysilane. The reaction of the chloro-functionalized MNPs with dithizone produced



SCHEME 1 Synthesis of MNPs/SiO<sub>2</sub>-DTZ-Pd

dithizone-functionalized Fe<sub>3</sub>O<sub>4</sub>. Finally, Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd was obtained via coordination of palladium with MNPs/ SiO<sub>2</sub>-DTZ surface.

Catalyst characterization was performed using transmission electron microscopy, X-ray diffraction, Fouriertransform infrared spectroscopy, energy dispersive X-ray spectroscopy, vibrating sample magnetometer and scanning electron microscopy. XRD pattern of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd sample is shown in Figure 1. In the corresponding curve, six characteristic diffraction peaks appeared at  $2\theta = 30.1(220)$ , 35.3(311), 43.0(400), 53.4(422), 56.9(511) and 62.5(440). Besides the characteristic peaks of Fe<sub>3</sub>O<sub>4</sub> core, three additional peaks can be observed at  $2\theta = 39.3(111)$ , 45.49(110) and 67.1(100), are indexed to Pd(0) indicating the presence of Pd(0)in the prepared nanocatalyst.<sup>[16]</sup>

The shape and size of the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd were determined by SEM (Figure 2). Moreover, the TEM image of the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd catalyst shows that the functionalized magnetic nanoparticles possess almost spherical morphology (Figure 3).

The elemental composition of the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd catalyst performed by EDS analysis, which the results shown in Figure 4. The distribution of the elements (atomic percent) in the complex was determined as Si = 1.49%, Fe = 29.15%, O = 62.38% and Pd = 5.59%. Exact loading of Pd on the



FIGURE 1 XRD pattern of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pdnanoparticles



Applied

SEM HV: 30.0 kV IRA3 TESCA v field: 5.00 um M MAG: 55.4 kx ): 01/17/15

FIGURE 2 SEM images of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd



FIGURE 3 TEM images of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd

magnetic nanoparticles was determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES) that was to be 1.65 mmol  $g^{-1}$ .

The magnetic properties of MNPs/SiO<sub>2</sub>-DTZ Pd were determined using vibrating sample magnetometry (Figure 5). It can be seen that the magnetic saturation values of the catalyst is 51 emu  $g^{-1}$ . The decrease of the saturation magnetization suggests the presence of some palladium particles on the surface of the magnetic supports.<sup>[17]</sup>

The palladium catalyzed C-C and C-N bond forming reactions are of the most important transformations in organic reactions. The catalytic activity of MNPs/SiO<sub>2</sub>-DTZ-Pd was evaluated in the C-C coupling reaction of aryl halides with triphenyltinchloride (Stille reaction), butyl acrylate (Heck reaction) and amination of aryl halides with aqueous ammonia.



FIGURE 4 EDS analysis of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd



FIGURE 5 Magnetization curves for Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd

# **2.10** | Evaluation of the catalytic activity of MNPs/SiO<sub>2</sub>-DTZ-Pd through the Stille reaction

Initially, we employed iodobenzene and triphenyltinchloride in PEG as a solvent in the presence of  $Na_2CO_3$  as base at 80 °C as model substrates for the optimization of the reaction conditions (Scheme 2).

Different parameters were investigated for this model reaction including the use of different molar ratio of catalyst, variety of solvents, bases, and temperature (Table 1). In order to explore the role of this nanocatalyst in the outcome of C-C coupling reaction, several experiments were carried out using different amounts of catalyst (Table 1, entries 1–4). The resulting optimum amount of the catalyst was (0.005 g) of MNPs/SiO<sub>2</sub>-DTZ-Pd (Table 1, entry 3), which increasing of this amount did not show any significant change in yield.

When the reaction was carried out in different solvents such as Dioxane, DMF, DMSO, water and PEG under the same reaction conditions, the products were obtained in poor to good yields of 40%, 75%, 68%, 86% and 96%



SCHEME 2 Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-PdcatalyzedStille reaction

**TABLE 1**C-C coupling of iodobenzenewithtriphenyltin chloride inthe presence of  $Fe_3O_4/SiO_2$ -DTZ-Pd under various conditions

Entry	Solvent	Base (mmol)	Catalyst (mg)	Temp (°C)	Time (min)	Yield (%)
1	PEG	Na <sub>2</sub> CO <sub>3</sub>	0	80	24 h	0
2	PEG	Na <sub>2</sub> CO <sub>3</sub>	2	80	25	45
3	PEG	Na <sub>2</sub> CO <sub>3</sub>	5	80	25	92
4	PEG	Na <sub>2</sub> CO <sub>3</sub>	7	80	25	96
5	DMF	Na <sub>2</sub> CO <sub>3</sub>	5	80	25	75
6	DMSO	Na <sub>2</sub> CO <sub>3</sub>	5	80	25	68
7	Dioxane	Na <sub>2</sub> CO <sub>3</sub>	5	80	25	40
8	$H_2O$	Na <sub>2</sub> CO <sub>3</sub>	5	80	25	86
9	PEG	КОН	5	80	25	54
10	PEG	NaOH	5	80	25	50
11	PEG	K <sub>2</sub> CO <sub>3</sub>	5	80	25	85
12	PEG	Et <sub>3</sub> N	5	80	25	35
13	PEG	Na <sub>2</sub> CO <sub>3</sub>	5	Rt	5 h	Trace
14	PEG	Na <sub>2</sub> CO <sub>3</sub>	5	60	5 h	68
15	PEG	Na <sub>2</sub> CO <sub>3</sub>	5	100	25	95

<sup>a</sup>Reaction conditions: iodobenzene (1 mmol), triphenyltin chloride (0.5 mmol), base (3 mmol), Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd (.0005 g), solvent (2 mL) at 80 °C.

(Table 1, entries 4–8). After the solvent screening, PEG was chosen as solvent of reaction. Next studies focused on the influence of the base on the reaction. The reactions were carried out under similar conditions using different bases such as Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, KOH, NaOH and Et<sub>3</sub>N; the obtained yields were 96%, 85%, 54%, 50% and 35%, respectively (Table 1, entries 9-12). As shown in Table 1, it was found that Na<sub>2</sub>CO<sub>3</sub> was an effective base for the reaction with the highest yield. To investigate the effect of temperature on the outcome of coupling reaction, we performed the reaction at difference temperatures: room temperature, 60, 80 and 100 °C (Table 1, 13-15). Based on these obtained results in Table 1, temperature of 80 °C was selected. Next, using the optimized procedure, triphenyltinchloride and various aryl halides possessing both electron releasing and electron-withdrawing groups were employed. As shown in Table 2, reactions of aryl iodides were done in short time, while the aryl bromides and aryl chlorides required longer reaction times.

# **2.11** | Evaluation of the catalytic activity of MNPs/SiO<sub>2</sub>-DTZ-Pd through the Heck reaction

The next part of the study focused on the utility of this catalyst in Heck reaction. To standardize the reaction conditions, a series of reactions were performed using several bases and solvents, and different temperatures and molar ratio of catalyst (Table 3). Initially, the experiment was performed using

Entry	X	R	Time (min)	Yield (%)	<b>M.p.</b> (°C)
1	Ι	Н	25	92	67–69 <sup>[18]</sup>
2	Ι	4-OCH <sub>3</sub>	55	95	86-88 <sup>[19]</sup>
3	Ι	4-CH <sub>3</sub>	75	90	45-47 <sup>[20]</sup>
4	Br	Н	30	88	67–69 <sup>[18]</sup>
5	Br	4-CH3	65	93	44-47 <sup>[20]</sup>
6	Br	4-Cn	60	95	83-87 <sup>[20]</sup>
7	Br	4-oh	55	87	161–163 <sup>[18]</sup>
8	Br	4-cl	45	90	73–76 <sup>[21]</sup>
9	Br	4-Cho	145	80	52-55 <sup>[18]</sup>
10	Br	4-NO <sub>2</sub>	50	93	112–115 <sup>[21]</sup>
11	Cl	Н	180	89	67-70 <sup>[18]</sup>

<sup>a</sup>Reaction condition: Aryl halide (1 mmol), Ph<sub>3</sub>SnCl (0.5 mmol), Na<sub>2</sub>CO<sub>3</sub> (3 mmol), Cat. (5 mg), PEG (2 ml).

 
 TABLE 3
 C-C coupling of iodobenzenewithbutyl acrylate in the presence of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd under various conditions

Entry	Solvent	Base (mmol)	Catalyst (mg)	Temp (°C)	Time (min)	Yield (%)
1	PEG	K <sub>2</sub> CO <sub>3</sub>	2	100	240	36
2	PEG	K <sub>2</sub> CO <sub>3</sub>	5	100	30	55
3	PEG	K <sub>2</sub> CO <sub>3</sub>	7	100	30	93
4	PEG	K <sub>2</sub> CO <sub>3</sub>	10	100	20	95
5	DMF	K <sub>2</sub> CO <sub>3</sub>	7	100	30	84
6	DMSO	K <sub>2</sub> CO <sub>3</sub>	7	100	30	78
7	Dioxane	$K_2CO_3$	7	100	30	Trace
8	$H_2O$	K <sub>2</sub> CO <sub>3</sub>	7	100	30	80
9	PEG	KOH	7	100	30	75
10	PEG	NaOH	7	80	30	70
11	PEG	K <sub>2</sub> CO <sub>3</sub>	7	100	30	93
12	PEG	Et <sub>3</sub> N	7	100	30	65
13	PEG	Na <sub>2</sub> CO <sub>3</sub>	7	100	30	88
14	PEG	K <sub>2</sub> CO <sub>3</sub>	7	Rt	240	Trace
15	PEG	K <sub>2</sub> CO <sub>3</sub>	7	60	30	42
16	PEG	K <sub>2</sub> CO <sub>3</sub>	7	80	30	68
17	PEG	K <sub>2</sub> CO <sub>3</sub>	7	100	30	93

<sup>a</sup>Reaction conditions: iodobenzene (1 mmol)butyl acrylate (1.2 mmol), base (3 mmol), Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd (0.007 g), solvent (2 ml) at 100 °C.

iodobenzene (1.0 mmol) butyl acrylate (1.2 mmol),  $K_2CO_3$  (3.0 mmol) and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd (0.007 g) in PEG as solvent at 100 °C (Scheme 3).

Initially, the amount of catalyst was optimized (Table 3, entries 1–4); it was observed that the best results were obtained with 0.007 g of catalyst (Table 3, entry 3).



SCHEME 3 Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd catalysed Heck reaction

The reactivity of the catalyst in the presence of different bases was also investigated. Among the tested bases  $(Na_2CO_3, K_2CO_3, KOH, NaOH and Et_3N)$  the best choice was  $K_2CO_3$  due to the highest yield of product (Table 3, entry 11). Subsequently, the influence of different solvents was examined (Table 3, entries 5–8). Among the solvents examined, the highest yield was achieved when using PEG (Table3, entry 3). Next, effect of temperature on the outcome of reaction, the reaction was carried out at different temperatures such as room temperature, 60, 80 and 100 °C (Table 3, entries 14–17). Based on these obtained results, temperature of 100 °C was selected.

After optimizing the reaction conditions, the catalytic activity of MNPs/SiO<sub>2</sub>-DTZ-Pd for Heck reaction was explored with respect to various aryl halides and butyl acrylate, as listed in Table 4.

# **2.12** | Evaluation of the catalytic activity of MNPs/SiO<sub>2</sub>-DTZ-Pd through the *N*-arylation reaction

The activity of described catalyst was investigated through a reaction of aryl halides with  $NH_3.H_2O$  for amination reaction of various aryl halides. Initially, we examined the reaction of iodobenzene with aqueous ammonia (28%) in

**TABLE 4**C-C coupling reaction of aryl halides withtriphenyltinchloridecatalyzed by  $Fe_3O_4/SiO_2$ -DTZ-Pdat 100 °C

Entry	X	R	Alkene	Time (min)	Yield (%)	М.р. (°С)
1	Ι	Н	Butyl acrylate	30	92	Oil <sup>[22]</sup>
2	Ι	4-OCH <sub>3</sub>	Butyl acrylate	75	95	Oil <sup>[23]</sup>
3	Ι	4-CH <sub>3</sub>	Butyl acrylate	65	90	Oil <sup>[22]</sup>
4	Br	Н	Butyl acrylate	45	88	Oil <sup>[22]</sup>
5	Br	4-CH3	Butyl acrylate	110	93	Oil <sup>[22]</sup>
6	Br	4-Cn	Butyl acrylate	130	95	39-42 <sup>[22]</sup>
7	Ι	2-OCH <sub>3</sub>	Butyl acrylate	3.5 h	87	Oil <sup>[24]</sup>
8	Br	4-cl	Butyl acrylate	160	90	Oil <sup>[22]</sup>
9	Br	4-NO <sub>2</sub>	Butyl acrylate	190	80	57–61 <sup>[22]</sup>
10	Br	3-Br-pyridin	Butyl acrylate	90	83	Oil <sup>[22]</sup>
11	Cl	4-Cn	Butyl acrylate	14 h	90	40-42 <sup>[22]</sup>
12	Cl	Н	Butyl acrylate	11 h	93	Oil <sup>[22]</sup>

<sup>a</sup>Reaction condition: Aryl halide (1 mmol), butyl acrylate (0.5 mmol),  $K_2CO_3$  (3 mmol), Cat. (7 mg), PEG (2 ml).

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differentsolvents and various catalytic amounts of MNPs/ SiO<sub>2</sub>-DTZ-Pd (Table 5). It was observed that the best results were obtained with 0.005 g of catalyst (Table 5, entry 2). Then, the reaction was performed using different solvents that the results are shown in Table 5. After optimizing the reaction conditions, the amination reactions of various arylhalides with NH<sub>3</sub>.H<sub>2</sub>O were tested. Results have been summarized in Table 6.

For practical applications of heterogeneous systems, the recyclability of a catalyst is an important factor. The recyclability of  $Fe_3O_4/SiO_2$ -DTZ-Pd was studied in the coupling reaction of iodobenzene with butylacrylate and amination reaction of iodobenzene with aqueous ammonia. In order to reuse the catalyst, after reaction completion, it was separated by a magnet and washed several times with ethyl acetate. Then, it was dried in an oven at 50 °C and used in the next run. The results show that this catalyst can be reused 5 times without any significant loss in activity performance (Figure 6). This result also demonstrated that the palladium leaching of the catalyst was low.

 TABLE 5
 Amination of iodobenzene with aqueous ammonia in the presence of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-DTZ-Pd under various conditions

Entry	Solvent	Catalyst (mg)	Time (h)	Yield %
1	-	0.003	9	70
2	-	0.005	5	90
3	-	0.007	4	92
4	-	0.005	5	90
5	DMF	0.005	5	65
6	EtOH	0.005	5	77

Reaction conditions: iodobenzene: 1 mmol, aqueous ammonia: 2 ml, catalyst: 0.005 g, at 60 °C.

**TABLE 6** Aminationofaryl halides with aqueous ammonia in thepresence of  $Fe_3O_4/SiO_2$ -DTZ-Pd at 60 °C

Entry	Х	R	Time(h)	Yield (%)	M.p. (°C)
1	Ι	Н	5	90	Oil <sup>[25]</sup>
2	Ι	4-OCH <sub>3</sub>	7	91	56-58 <sup>[26]</sup>
3	Ι	4-CH <sub>3</sub>	6.5	88	43-45 <sup>[25]</sup>
4	Br	Н	7	85	Oil <sup>[25]</sup>
5	Br	4-CH3	8	93	43-45 <sup>[25]</sup>
6	Br	4-Cn	5	95	86-88 <sup>[25]</sup>
7	Br	4-Cho	5	84	68-70 <sup>[27]</sup>
8	Br	4-cl	8.5	96	68-70 <sup>[26]</sup>
9	Br	4-NO <sub>2</sub>	5	94	146–148 <sup>[26]</sup>
10	Br	1-Br-naphthalene	11	80	47-49 <sup>[25]</sup>

Reaction conditions: Aryl halides: 1 mmol, aqueous ammonia: 2 ml, catalyst: 0.005 g, at 60 °C.



**FIGURE 6** Recyclability of  $Fe_3O_4/SiO_2$ -DTZ-Pd in the coupling of iodobenzene (1.0 mmol) with (a) butyl acrylate (1.2 mmol) and (b) aqueous ammonia (2.0 mL) under reaction conditions

### **3** | CONCLUSIONS

In conclusion,  $Fe_3O_4/SiO_2$ -DTZ-Pd was synthesized and tested to evaluate its catalytic activity in Heck, Stille, and *N*-arylation reactions. Under the optimized conditions, the catalyst displayed excellent catalytic activity in delivering the desired products in good to excellent yields. This catalyst was characterized by several techniques such as XRD, VSM, TEM, SEM, EDS and ICPOES.

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