Design of Palladium(II) Chloride-supported-*N*-(dipyridine-2-ylmethyl)-3-(silica-magnetite)propan-1-amine and its Application on the Cross-coupling

M. Zarei[a],*, M.A. Zolfigol[a],*, A.R. Moosavi-Zare[b],* and E. Noroozizadeh

[a]*Depatment of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683*
[b]*Sayyed Jamaleddin Asadabadi University, Asadabad, 6541861841, Iran*

In this work, palladium(II) chloride-supported-*N*-(dipyridine-2-ylmethyl)-3-(silica-magnetite)propan-1-amine (nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$) as a new nanostructured catalyst was prepared and its structure completely studied by different techniques and then successfully tested on Heck and Suzuki reactions.

INTRODUCTION

High activity and facile recovery are two important parameters for designing the expensive catalysts in terms of green chemistry [1-2]. Coupling reaction, where two hydrocarbon fragments are coupled with the aid of a metal catalyst, has become a hot issue for its development and applications. Thus, nano catalysts which can be separated quickly and easily from the reaction medium are significant. Therefore, designing nano magnetic catalysts which can be collected easily with magnet are of great importance [3].

Therefore, for scientific and industrial goals, there are new achievements in coupling reactions in terms of developing Pd systems leading to increase activity in different coupling reactions [4]. Applications of nano-magnetic complexes are in C-C coupling of aryl halides with alkenes in the presence of base, called Heck reaction [5-7], or aryl halides with organoboron, called Suzuki reaction [8-11]. Coupling reactions have a considerable role in pharmaceutical manufacture due to their remarkable efficacy in the synthesis of natural products, organic products and bioactive compounds such as anti- asthmatic, morphine and antimicrobial (Fig. 1) [12-15].

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*Corresponding author. E-mail: mahmoud8103@yahoo. com

Catalysts are classified as heterogeneous and homogeneous. In terms of separation, homogeneous catalysts are of more interest due to being collected easier than heterogeneous in solution, although the reaction time and yield reaction for homogeneous are longer and lower, respectively. Nanotechnology helps scientist to design heterogeneous catalysts with no problems mentioned because the ratio of surface to volume is increased in nanomaterial improving the physical connection between reactants and catalyst and consequently increases the catalytic activity [16]. Nowadays, magnetic catalysts which can be easily collected from the medium of the reaction and then recovered and recycled have become so significant [17-18].

These reactions are mainly metal-catalysts reactions of organohalide with olefin which are important for organic synthesis. Because organoborane and benzoic acid as comparison with aryl halide are less toxic and more stable, aryl halides are the best substituent for coupling reactions as a substituent has not been reported for Heck reaction [19, 20].

Herein, we have reported C-C coupling reaction of aryl halides with activated alkenes (Heck reaction) and palladium-catalysed cross coupling reaction of organoboronic acid with aryl halides (Suzuki reaction) using palladium(II) chloride-supported-*N*-(dipyridine-2-
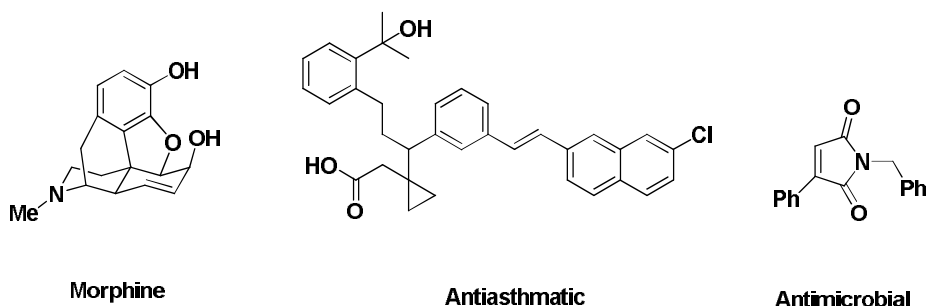
Fig. 1. Some bioactive compounds prepared by cross coupling reactions.
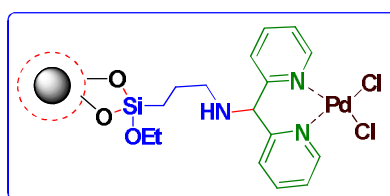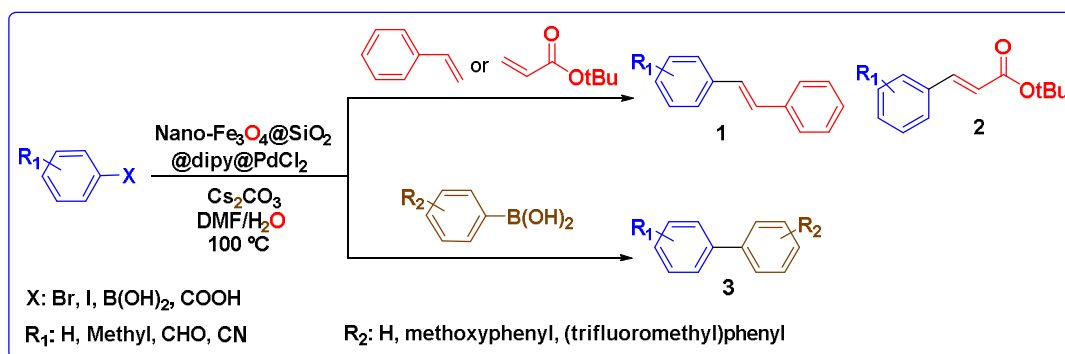

Fig. 2. The structure of nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$.

Scheme 1. Cross coupling reactions catalyzed by nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$

ylmethyl)-3-(silica-magnetite)propan-1-amine (nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$) as a new nanostructured and reusable catalyst at 100 °C (Fig. 2 and Scheme 1) .

EXPERIMENTAL

Preparation of Nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$

At first, magnetic nanoparticles Fe_3O_4 and Fe_3O_4@SiO_2

were synthesized according to previous literature [21]. Silica coated magnetic nanoparticles put under vacuum to dry. Dry particles (1 g) was dispersed in dry toluene (50 ml) and sonicated for 30 min.

(3-aminopropyl) triethoxysilane (3.5 ml, 16.02 mmol) was added drop wise to the suspended solid nanoparticles under mechanical stirring. The reaction was refluxed for 20 h. After refluxing, the
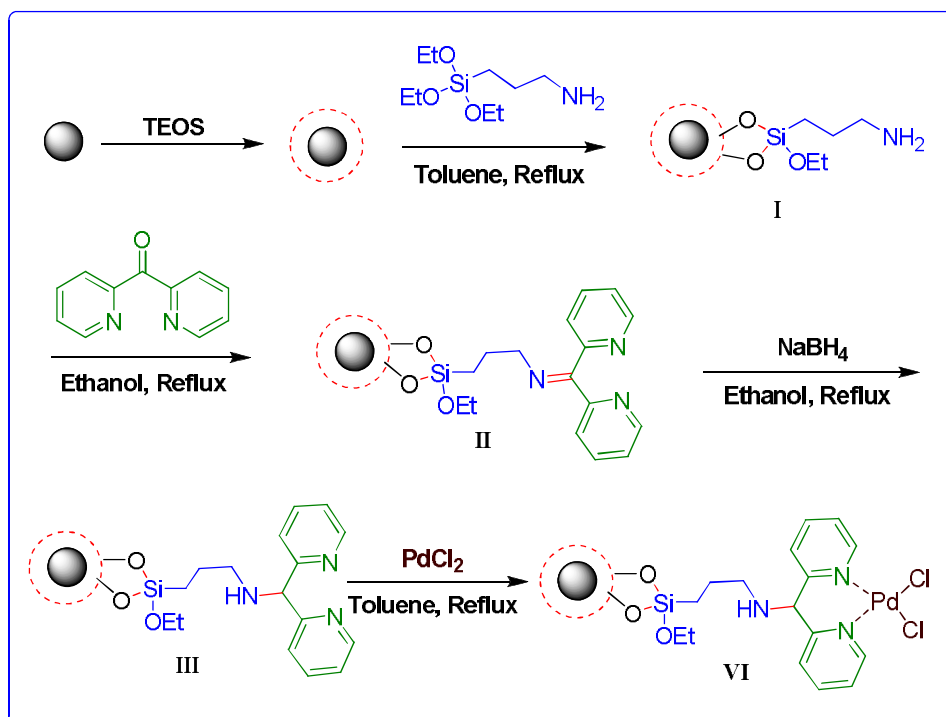
Scheme 2. Preparation of nano-Fe$_3$O$_4$@SiO$_2$@dipy@PdCl$_2$

nanoparticles were cooled down and then separated by a magnet. Then, the nanoparticles (I) were washed three times with anhydrous ethanol and then dried under vacuum. I (3 g) was suspended in dry ethanol (50 ml), and after sonication for 15 min, di(pyridin-2-yl) methanone (1.84 g, 10 mmol) was added to the reaction mixture and heated at under reflux conditions for 2 days. After cooling down to room temperature, the obtained particles were separated magnetically, washed 3 times with dry ethanol, and dried under a vacuum for 24 h to give II, and then, NaBH$_4$ (0.0197 g, 0.52 mmol) was added to II in ethanol (15 ml) and refluxed for 24 h to afford III. The nanoparticles (III) were washed (3 × 10 ml) with ethanol and then dried under vacuum. Dry nanoparticles III (1 g) was sonicated in dry toluene (15 ml) for 30 min. Then, PdCl$_2$ (0.6 mmol, 0.1 g) in toluene (15 ml) was added and the mixture was refluxed for 12 h under argon atmosphere. The resulting product (IV) was separated by an external magnet and washed with water (1 × 10 ml) and methanol (3 × 10 ml), respectively, and then dried under vacuum.

General Procedure for the Heck Reaction

A round-bottomed flask (10 ml) was charged with iodobenzene (1 mmol), styrene (1.2 mmol) in DMF/H$_2$O as solvent (5.0 ml, v/v = 1:1), Cs$_2$CO$_3$ (1.5 mmol) and nano-Fe$_3$O$_4$@SiO$_2$@dipy@PdCl$_2$ (0.05 g, containing 2.2 × 10^{-4} g, 0.0012 mmol of Pd) and connected to a reflux condenser. The reaction mixture was stirred for the required period of time at 100 °C to reaction completion, as monitored by TLC. The reaction mixture was then cooled at room temperature and the catalyst easily collected by means of a magnet to reuse it for another reaction. The residue of the reaction was extracted with Et$_2$O (3 × 5 ml). The solvent was evaporated to afford the desired product in an almost pure state. Further purification has been performed by using column chromatography over silica gel that eluted with n-hexane/ethyl acetate (10:1) to give the pure expected products.

General Procedure for the Suzuki Reaction

A round-bottomed flask (10 ml) was charged with iodobenzene (1 mmol), phenylboronic acid (1 mmol) in

DMF/H_2O as solvent (5.0 ml, v/v = 1:1), Cs_2CO_3 (1.5 mmol) and nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$ (0.05 g, containing 2.2×10^{-4} g, 0.0012 mmol of Pd) and connected to a reflux condenser. The reaction mixture was stirred at 100 °C to completion, as monitored by TLC. The reaction mixture was cooled at room temperature and the catalyst was removed from the solution using a magnet to reuse it for another reaction. Finally, the residue of the reaction was subsequently purified by column chromatography over silica gel using n-hexane/ethyl acetate (13:1) to afford the desired product.

Spectral Data Analysis for Compounds

(E)-1,2-diphenylethene (1a). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.14 (d, *J* = 12 Hz, 2H), 7.26-7.3 (dt, 2H), 7.36-7.4 (m, 4H), 7.52-7.55 (dd, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 126.57, 127.7, 128.71, 137.33.

Butyl cinnamate (2a). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.69-0.73 (t, *J* = 12 Hz, 3H), 1.14-1.23 (m, 2H), 1.4-1.47 (m, 2H), 3.93-3.96 (t, *J* = 12 Hz, 2H), 6.17-6.2 (d, *J* = 12 Hz, 1H), 7.11-7.13 (m, 3H), 7.26-7.28 (dd, *J* = 8Hz, 2H), 7.4-7.44 (d, *J* = 16 Hz, 1H), 7.73 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.49, 18.94, 30.52, 30.95, 36.16, 64.08, 118.18, 127.8, 128.87, 130.04, 144.26, 162.34, 166.73.

(E)-1,2-diphenylethene (1a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12-7.13 (d, *J* = 9 Hz, 2H), 7.25-7.3 (m, 2H), 7.35-7.4 (m, 4H), 7.52-7.54 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 126.57, 127.69, 128.75, 137.33.

Butyl cinnamate (1a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.69-0.72 (t, *J* = 9 Hz, 3H), 1.15-1.21 (m, 2H), 1.39-1.45 (m, 2H), 3.92-3.96 (t, *J* = 12 Hz, 2H), 6.17-6.21 (d, *J* = 12 Hz, 1H), 7.11-7.12 (m, 3H), 7.26-7.28 (dd, *J* = 8Hz, 2H), 7.39-7.43 (d, *J* = 16 Hz, 1H), 7.73 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.49, 18.96, 30.52, 30.95, 36.16, 64.08, 118.01, 127.8, 128.87, 130.04, 134.15, 144.26, 162.31, 166.7.

1,1'-Biphenyl (3a). ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.12-7.13 (d, *J* = 9 Hz, 2H), 7.25-7.3 (m, 2H), 7.35-7.4 (m, 4H), 7.52-7.54 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 126.57, 127.69, 128.75, 137.33.

4-Methyl-1,1'-biphenyl (3d). ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.29 (s, 3H), 6.57 (s, 1H), 7.14 (s, 3H), 7.67 (s, 3H), 7.94 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.15, 126.19, 128.12, 134.16, 134.36, 134.44, 134.5, 134.58,

139.39.

4-(Trifluoromethyl)-1,1'-biphenyl (3c). ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.5107.52 (m ,1H), 7.56-7.62 (m, 1H), 7.72-7.76 (m, 2H), 7.79-7.81 (d, *J* = 6 Hz, 1H), 7.87-7.89 (d, *J* = 6 Hz, 1H), 7.95-7.97 (d, *J* = 6 Hz, 1H), 8.01-8.05 (t, *J* = 12 Hz, 1H), 8.1-8.17 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 123.87, 123.91, 125.37, 125.77, 127.02, 127.48, 128.45, 129.12, 134.63.

RESULTS AND DISCUSSION

Characterization Methods

The structure of the new magnetite nano-catalyst was characterized by several techniques including Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermal gravimetric analysis (TGA), differential thermal gravimetric (DTG), scanning electron microscope (SEM), transmission electron microscopy (TEM), Energy dispersive X-ray analysis (EDX) and inductively coupled plasma (ICP), X-Ray photoelectron spectroscopy (XPS) and vibrating sample magnetometry (VSM) analyses.

Fe_3O_4 was coated with a layer of silica with tetraethyl orthosilicate (TEOS). Silanation of the silica-coated magnetite nanoparticles (SMNPs) was performed with 3-aminopropyl triethoxysilane to obtain compound I. By the reaction of I with di(pyridin-2-yl)methanone II was prepared and then reduced with $NaBH_4$ to give III. In the last step, $PdCl_2$ was added to the reaction to afford nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$ (Scheme 2).

FT-IR spectra of compounds (II), (III) and the prepared catalyst have investigated (Fig. 3). A broad peak near 1000-1100 cm^{-1} could be related to Si-O stretching of silica coated magnetite nanoparticles. The peak at 1588 cm^{-1} concerns to stretching mode of C=N bond confirming C=N double bond in II which is removed in compound III. The peak at 1639 cm^{-1} is related to C=N double bond in pyridine ring due to reaction with Pd shifted to lower frequency at about 1629 cm^{-1} in the catalyst.

FT-IR spectra of nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$ showed some peaks at 445, 584 and 631 cm^{-1} related to Pd-Cl pond confirming the presence of Cl in catalyst.

The structure of nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$ was studied by energy dispersive X-ray analysis (EDX). The
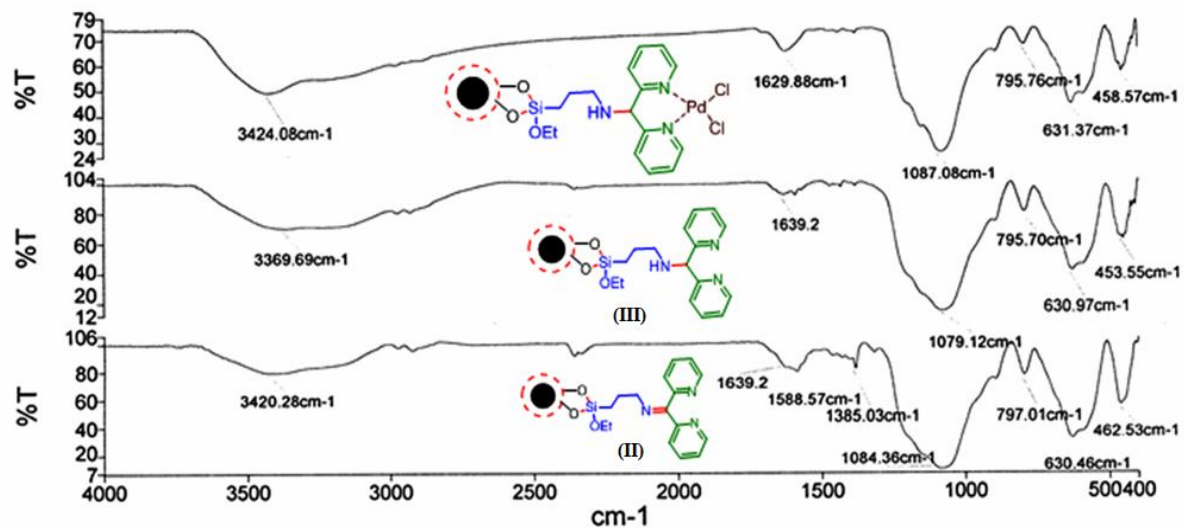
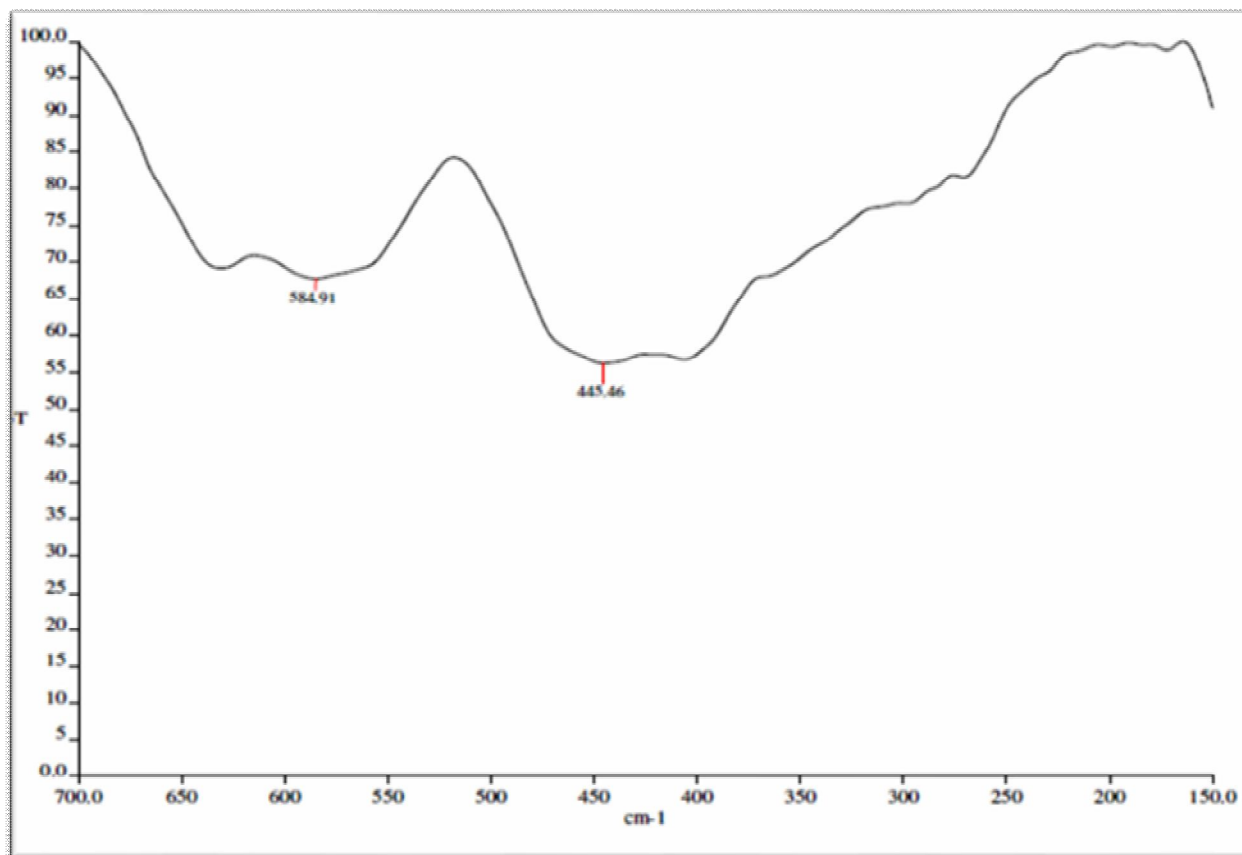**Fig. 3.** FT-IR spectra of (II), (III) and the prepared catalyst.

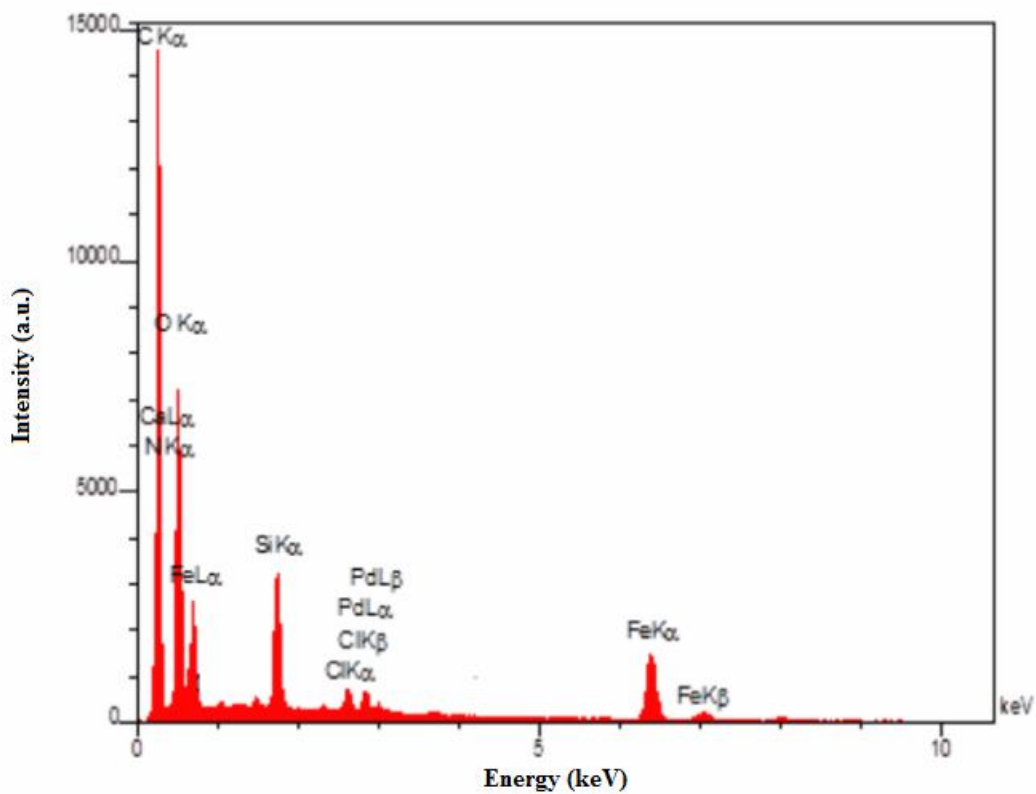**Fig. 4.** FT-IR spectra of nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$.

Fig. 5. EDX analysis of the nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$.
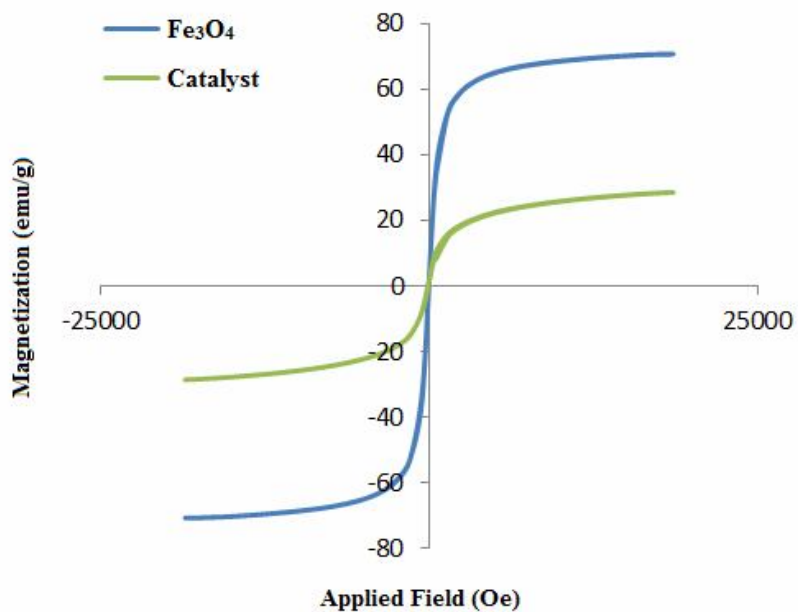

Fig. 6. The vibrating sample magnetometer (VSM) of Fe_3O_4 in comparison with catalyst.
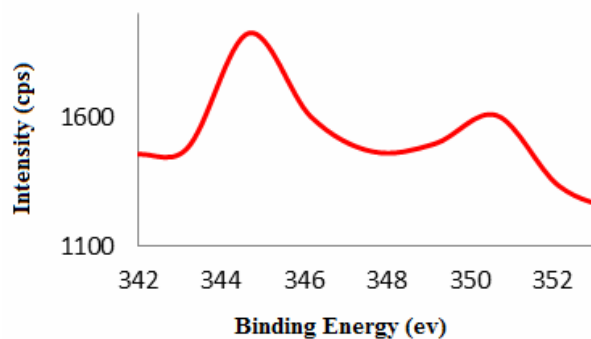
Fig. 7. XPS spectra of nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$.
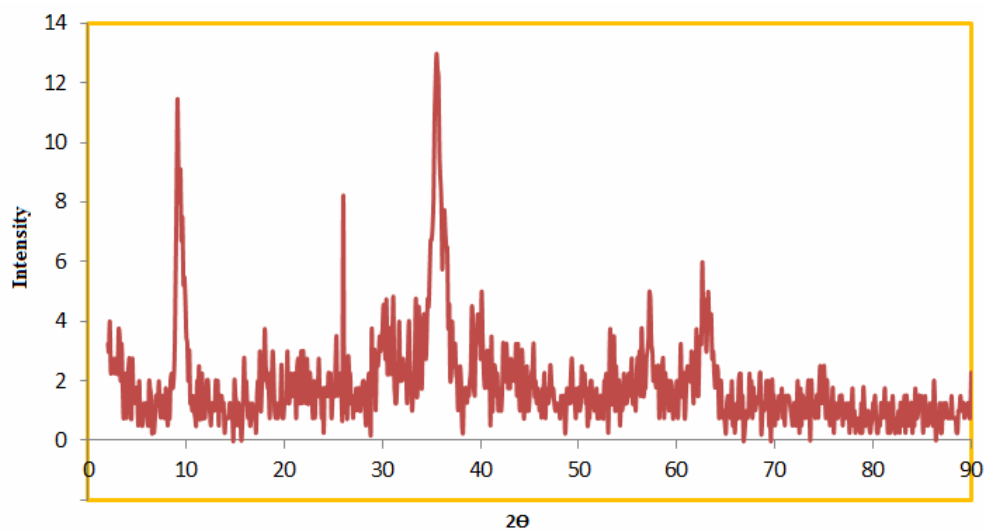
Fig. 8. XRD diagram of nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$.

Table 1. XRD Data for Nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$

Entry	$2\varTheta$	Peak width (degree)	Size (nm)	Inter planar distance (nm)
1	9.1	0.7	13.86	0.98
2	26	0.1	81.1	0.34
3	35.5	0.7	12.5	0.13
4	40.1	0.1	14.8	0.12
5	57.2	0.3	30	0.16
6	62.6	0.4	23.7	0.14
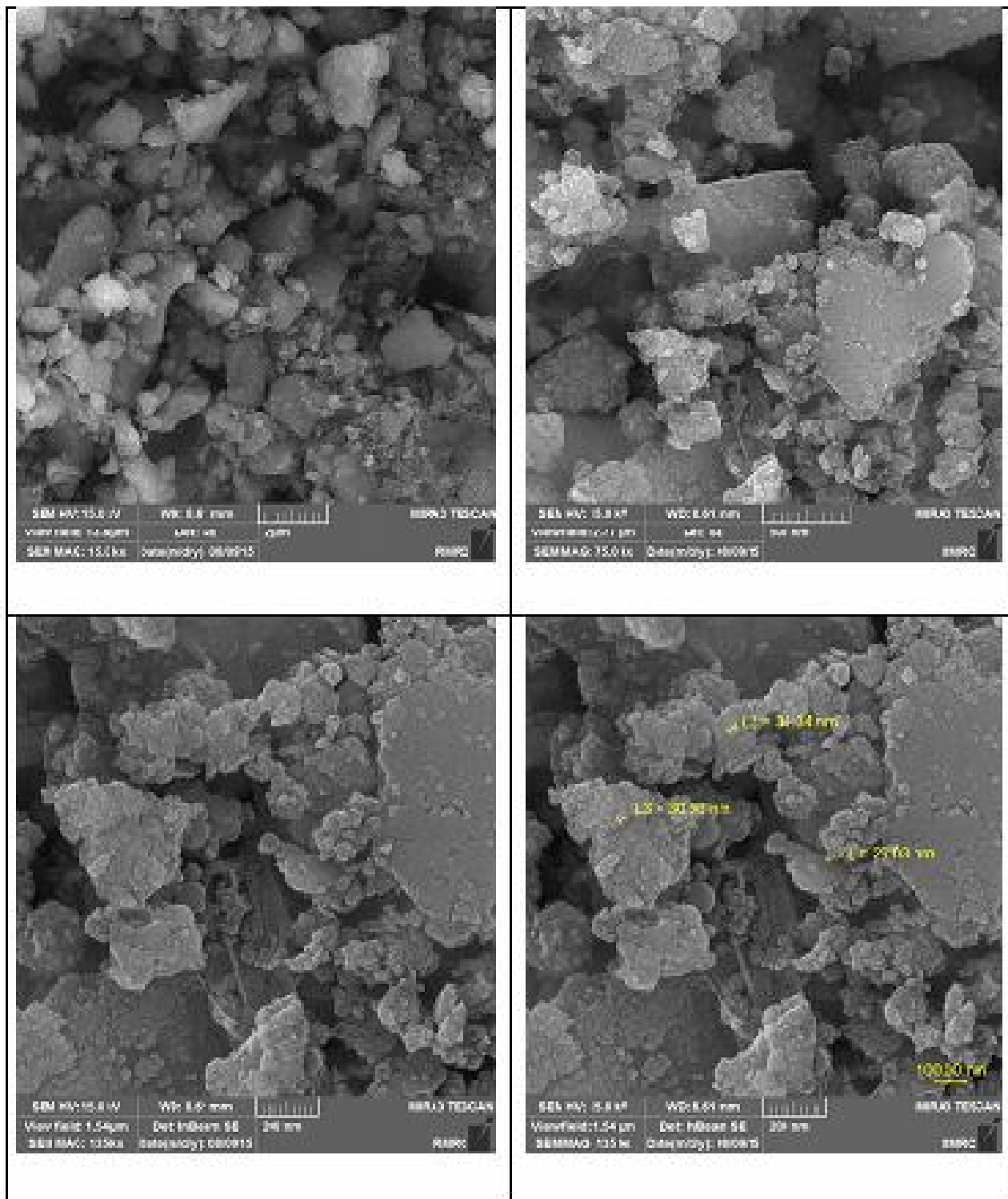
Fig. 9. SEM images of nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$.
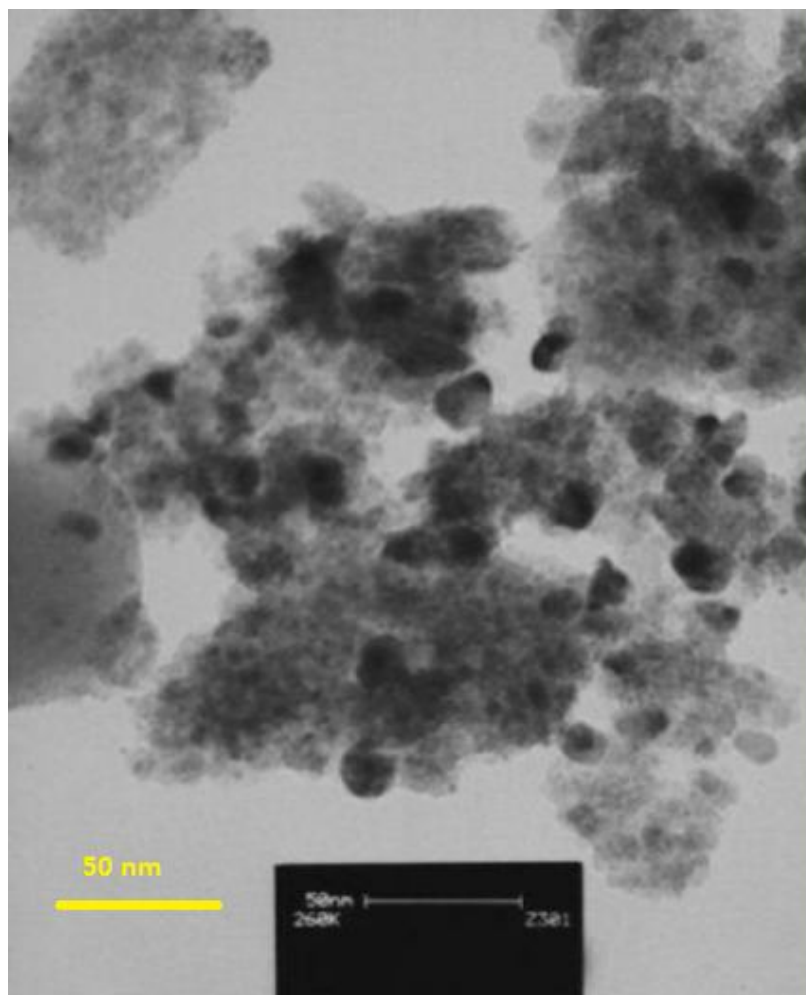
Fig. 10. TEM images of nano-Fe$_3$O$_4$@SiO$_2$@dipy@PdCl$_2$.

result was acceptable with expected elements such as iron, silicon, oxygen, chlorine, carbon, nitrogen and palladium. EDX analysis of the nano-Fe$_3$O$_4$@SiO$_2$@dipy@PdCl$_2$ is shown Fig. 5.

Magnetic measurements of the Fe$_3$O$_4$ nanoparticles and nano-Fe$_3$O$_4$@SiO$_2$@dipy@PdCl$_2$ with Pd were investigated at room temperature by using a vibrating sample magnetometer (VSM). Based on magnetization curves, the saturation of the obtained catalyst dropped from 70.7 emu g^{-1} (Fe$_3$O$_4$) to 28.6 emu g^{-1} for the catalyst. This reduction in saturation accounts for the surface coating on Fe$_3$O$_4$ nanoparticles that interact with nano-catalyst.

Inductively, coupled plasma optical emission

spectroscopy (ICP/OES) analysis of the catalyst showed that the weight percentage of Pd in the catalyst was 4.3 wt%.

X-ray photoelectroscopy (XPS) technique was used to determine the oxidation state of the Pd surface in nanocatalyst. The XPS spectrum of Pd is shown in Fig. 7. The binding energy showed the doublet peak at 344 ev (3d$_{5/2}$) and 350.7 ev (3d$_{3/2}$). This result could be attributed to the Pd (0) oxidation state. This result is consistent with previously reported values in the literature [22].

The X-ray diffraction (XRD) pattern of the catalyst was also investigated (Fig. 8). The size of the catalyst was calculated using the Debye-Scherrer's formula
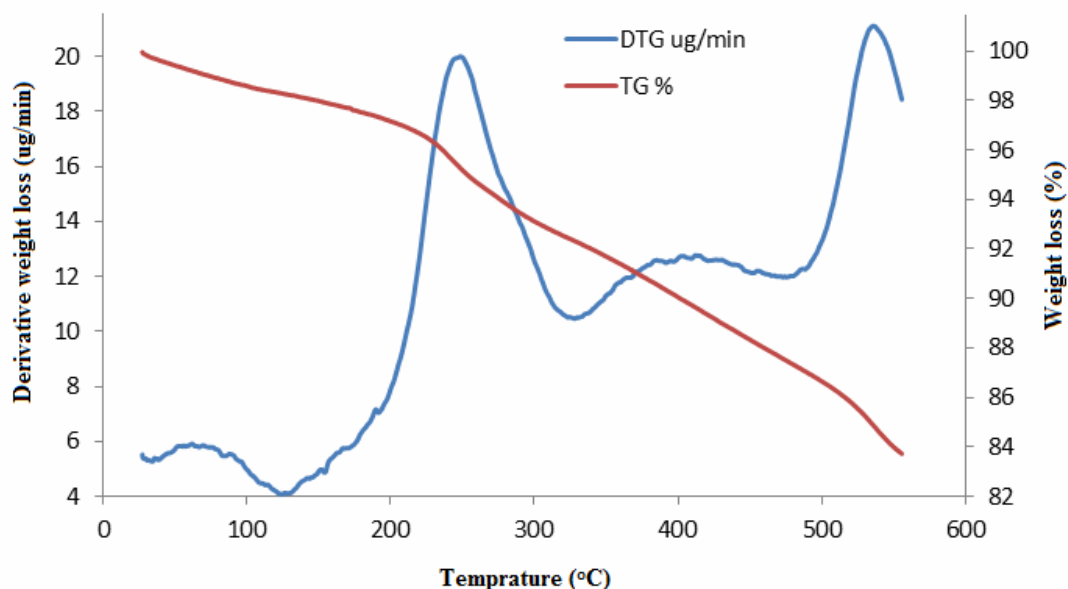
Fig. 11. TG/DTG catalyst nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$.

$D = K\lambda/(\beta Cos\theta)$, in which λ is X-ray wavelength, K is the Scherrer constant (0.9), β is the peak width of half-maximum, and θ is the Bragg diffraction angle. Inter planer distance of the particles was also calculated *via* the Bragg equation: $dhkl = \lambda/(2sin\theta)$, ($\lambda$: Cu radiation (0.154178 nm) was achieved. Obtaining crystallite sizes from various diffraction lines using the Debye-Scherrer's formula were found in the nanometer range (12.5-81.1 nm) (Table 1), which is in a good agreement with the transmission electron microscopy (TEM).

The scanning electron microscope (SEM) micrographs of nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$ was also studied. As showm in Fig. 9, particles of the catalyst are in nano scale which is in a good agreement with the size calculated through the Debye-Scherrer's equation.

Transmission electron microcopy (TEM) images of the catalyst are depicted in Fig. 10. According to this image, the catalyst was approximately 50 nm in size.

Thermal gravimetric (TG) of the catalyst was studied and given in Fig. 11. The thermal gravimetric (TG) and differential thermal gravimetric (DTG) of nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$ showed that it has been decomposed after 200 ºC.

To prove the activity of nano-Fe_3O_4@SiO_2@dipy@ $PdCl_2$ as new catalyst, we have tested it on Heck reaction. For this purpose, the reaction of iodobenzene with styrene was selected as the model reaction. At first, the coupling reaction was carried out in the presence of DMF/H_2O as solvent, Cs_2CO_3 as a base and catalyst (0.12% or 0.05 g) at 100 °C for 3 h which led to 95% yield of product (Table 2, entry 5). Different solvents such as DMF, water and toluene were investigated in this reaction. The higher yield was obtained with DMF/H_2O as shown in Table 2. Using different bases such as NaOH, NaOAc, Na_2CO_3 and Cs_2CO_3, and various amount of catalyst, the highest yield was obtained using Cs_2CO_3 in the presence of 0.12% or 0.05 g of catalyst.

Also, the activity of nano-Fe_3O_4@SiO_2@dipy@ $PdCl_2$ as new catalyst was tested in Suzuki reaction (Table 3). The coupling reaction of iodobenzene with phenyl bronic acid was chosen as model reaction. The model reaction was tested in the presence of DMF/H_2O as solvent, Cs_2CO_3 as a base and nano-Fe_3O_4@SiO_2@ dipy@$PdCl_2$ (0.12% or 0.05 g) as catalyst at 100 °C for 3 hours which led to 92% yield (Table 3, entry 5). Different solvents such as DMF, water and toluene were investigated in this reaction. The higher yield was

Table 2. Optimization of Base, Solvent and Catalyst in Heck Reaction[a]

Entry	Solvent	Base	Pd (%)	Time (h)	Yield (%)[b]
1	DMF	Cs_2CO_3	0.12	1	92
2	DMF	K_2CO_3	0.12	1.5	73
3	DMF	NaOH	0.12	2	68
4	DMF	NaOAc	0.12	3	55
5	DMF/H_2O	Cs_2CO_3	0.12	1	95
7	H_2O	Cs_2CO_3	0.12	2	74
8	Toluene	Cs_2CO_3	0.12	2	82
9	DMF/H_2O	Cs_2CO_3	0.1	2	84
10	DMF/H_2O	Cs_2CO_3	0.2	2	86

[a]Reaction condition iodobenzene (1 mmol), styrene (1.2 mmol), Cs_2CO_3 (1.5 mmol), solvent (5 ml). [b] Isolated yield.

Table 3. Optimization of Base, Solvent and Catalyst in the Suzuki Reaction[a]

Entry	Solvent	Base	Pd (%)	Time (h)	Yield (%)[b]
1	DMF	Cs_2CO_3	0.12	1	90
2	DMF	K_2CO_3	0.12	1.5	71
3	DMF	NaOH	0.12	3	68
4	DMF	NaOAc	0.12	4	61
5	DMF/H_2O	Cs_2CO_3	0.12	1	92
7	H_2O	Cs_2CO_3	0.12	1	75
8	Toluene	Cs_2CO_3	0.12	1.5	81
9	DMF/H_2O	Cs_2CO_3	0.1	2	86
10	DMF/H_2O	Cs_2CO_3	0.2	2	79

[a]Reaction condition: iodobenzene (1 mmol), phenyl bronic acid (1 mmol), Cs_2CO_3 (1.5 mmol), solvent (5 ml). [b]Isolated yield.
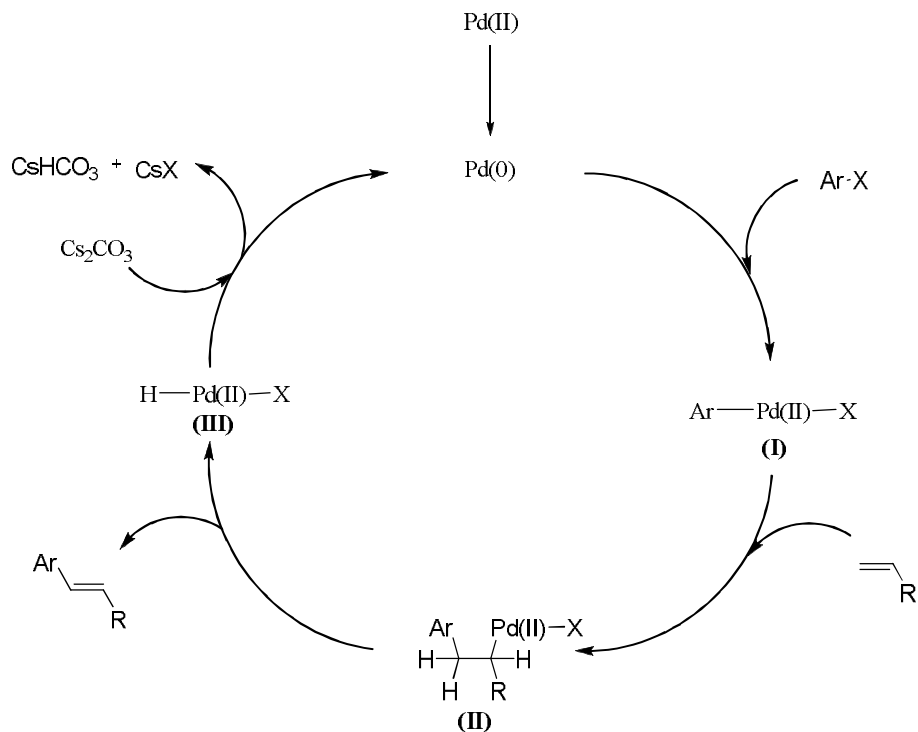
Table 4. Application of Nano-Fe$_3$O$_4$@SiO$_2$@dipy@PdCl$_2$ in the Heck Reaction

Entry	Ar-X	Olefine	Product	Time (h)	Yield (%)[a]
1	Iodobenzene	Styrene	1a	1	95
2	1-Iodo-4-methylbenzene	Styrene	1b	1	90
3	Bromobenzene	Styrene	1a	3	89
4	Iodobenzene	Butyl acrylate	2a	3	91
5	1-Iodo-4-methylbenzene	Butyl acrylate	2b	3	93
6	Bromobenzene	Butyl acrylate	2a	2.5	81
7	Phenylboronic acid	Styrene	1a	3	80
8	Phenylboronic acid	Butyl acrylate	2a	3.5	75
9	Benzoic acid	Styrene	1a	2.5	45
10	Benzoic acid	Butyl acrylate	2a	3	42
11	4-Bromo benzaldehyde	Styrene	1c	2.5	81

[a]Isolated yield.

Table 5. Application of Nano-Fe$_3$O$_4$@SiO$_2$@dipy@PdCl$_2$ in the Suzuki Reaction

Entry	Aryl halides	Aryl boronic acids	Product	Time (h)	Yield (%)[a]
1	Iodobenzene	Phenylboronic acid	3a	1	92
2	Iodobenzene	4-Methoxyphenylboronic acid	3b	1	89
3	Bromobenzene	4-Methoxyphenylboronic acid	3b	1	89
4	Iodobenzene	4-(Trifluoromethyl)phenylboronic acid	3c	1	94
5	Bromobenzene	Phenylboronic acid	3a	2	92
6	Iodobenzene	4-Methylphenylboronic acid	3d	3	91
7	Iodobenzene	4-(Trifluoromethyl)phenylboronic acid	3c	3	93
8	Bromobenzene	4-Methylphenylboronic acid	3d	3	93
9	Chlorobenzonitrile	Phenylboronic acid	3e	3	81
10	1-Bromo-4-methylbenzene	Phenylboronic acid	3f	3	86
11	1-Iodo-4-methylbenzene	Phenylboronic acid	3f	1.5	90

[a]Isolated yield.

Pd(II)

Pd(0)

Ar-X

CsHCO$_3$ + CsX

Cs$_2$CO$_3$

H—Pd(II)—X
(III)

Ar——Pd(II)—X
(I)

$$\overset{Ar}{\underset{R}{\diagdown}}$$

$$\underset{\underset{H \quad R}{|}}{\overset{Ar \quad Pd(II)-X}{\underset{H-\!\!\!\diagup\!\!\!-H}{}}}$$
(II)

Scheme 3. Proposed catalytic cycle for Heck reaction

Pd(II)

Pd(0)

Ar-X

Ar—R

RB(OH)$_2$ + CsOH

↓

RB(OH)$_3$Cs

Cs$_2$CO$_3$ + 2H$_2$O

↓

2CsOH + H$_2$CO$_3$

Ar——Pd(II)—R
(III)

Ar——Pd(II)—X
(I)

CsOH

B(OH)$_4^{\ominus}$

RB(OH)$_3^{\ominus}$

Ar——Pd(II)—OH
(II)

CsX
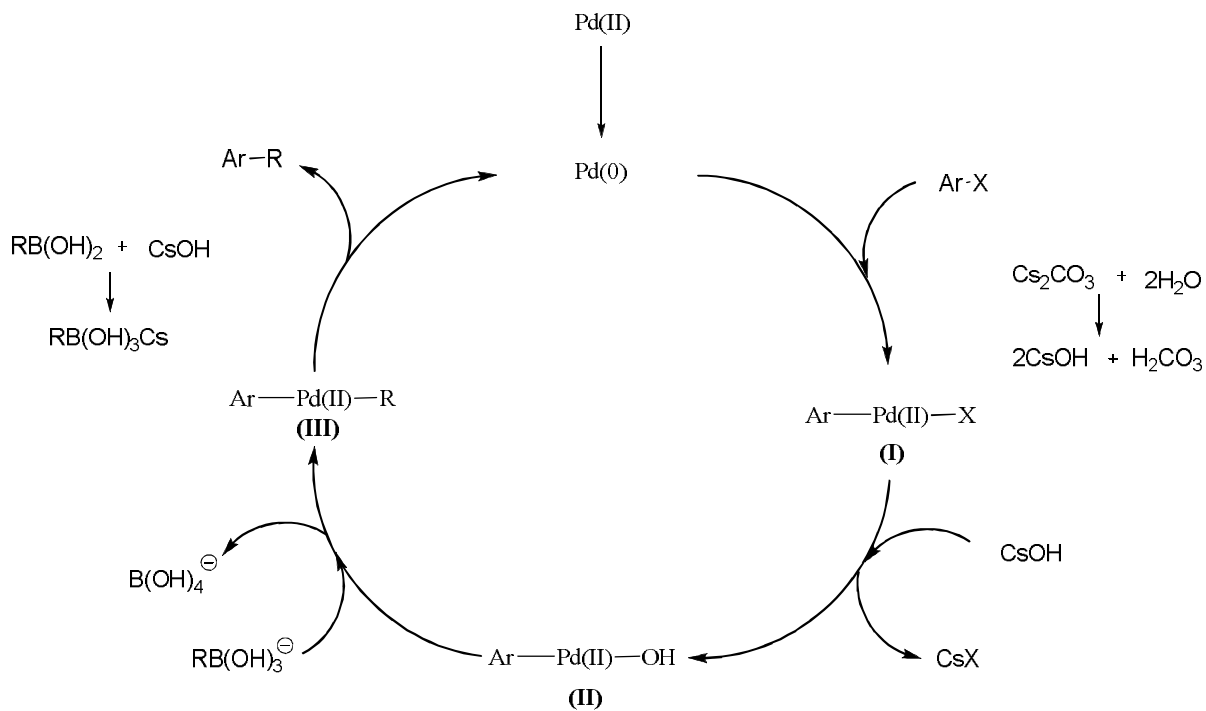
Scheme 4. Proposed catalytic cycle for the Suzuki reaction

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	1	2	3	4	5	6	7	8	9
■ The Heck reaction	95	94	92	92	90	88	85	83	79
■ The Suzuki reaction	92	91	89	89	86	84	81	78	75
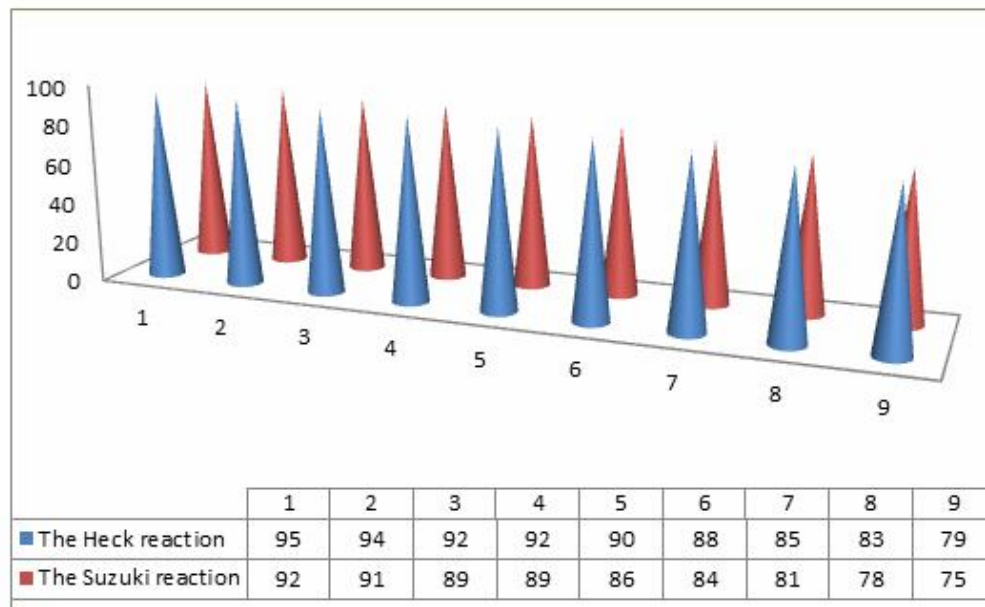
Fig. 12. Reusability of nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$.

observed with DMF/H_2O as shown in Table 3. Using various bases such as NaOH, NaOAc, Na_2CO_3 and Cs_2CO_3, and different amounts of catalyst, the highest yield was obtained using Cs_2CO_3 in the presence of 0.12% or 0.05 g of catalyst.

After the optimization of reaction condition, to investigate the generality of new catalyst in Heck and Suzuki reactions, various C (sp^2)-C (sp^2) coupling reactions were successfully tested using nano-Fe_3O_4@SiO_2@dipy@$PdCl_2$, and gave the corresponding products. In this regard, at first, the reaction of aryl halides or benzoic acid with various alkenes such as styrene and butyl acrylate was carried out.

In another study, cross coupling reaction between various aryl halides and different organoboronic acids using our palladium-nanocatalyst was also investigated (Table 5). As shown in Tables 4 and 5, all products were prepared in high yields and good reaction times.

In a proposed mechanism for Heck reaction, Pd (0) was prepared from Palladium precursor and reacted with arylaldehyde to give (I) *via* oxidative addition. In the next step, olefin compound was added to (I) to prepare (II) by

syn-addition and then *β*-hydride elimination of (II) afforded the expected products. In this cycle of catalytic reaction, Cs_2CO_3 as a base was reacted with (III) to prepare Pd (0) again by reductive elimination to proceed the reaction (Scheme 3). In another mechanism for Suzuki reaction, boronic acid derivative should be activated with a base and reacted with (II), which is produced from the reaction of (I) with CsOH by ligand exchange, to give (III) and finally, the expected product was prepared by reductive elimination (Scheme 4).

The reusability of the catalyst was also investigated. The reaction of iodobenzene and phenylboronic acid was selected as a model reaction and the coupling reaction was carried out. The catalyst was separated by an external magnet, washed with ethanol and dried. Regardless of the type of coupling, the results indicate that the catalyst can be utilized for nine runs without any significant loss of initial catalytic activity which can be ascribed to the high stability of the prepared catalyst.

CONCLUSIONS

We prepared and fully characterized palladium (II)

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chloride-supported-*N*-(dipyridine-2-ylmethyl)-3-(silica-magnetite)propan-1-amine (nano-Fe$_3$O$_4$@SiO$_2$@dipy@ PdCl$_2$) and successfully tested on C-C coupling reaction of aryl halides with activated alkenes (Heck reaction) and palladium-catalysed cross coupling reaction between organoboronic acid and aryl halides (Suzuki reaction) at 100 °C. Cleaner reaction profile and green substrate, short reaction times, high yields and easy recyclability of the catalyst are some advantages of this work.

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