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#### Applied Organometallic Chemistry

# Palladium supported on modified magnetic nanoparticles: a phosphine-free and heterogeneous catalyst for Suzuki and Stille reactions

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An efficient magnetic nanoparticle-supported palladium (Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd) catalyst is reported for the Suzuki cross-coupling and Stille reactions. This method provides a novel and much improved modification of the Suzuki and Stille coupling reactions in terms of phosphine-free catalyst, short reaction time, clean reaction and small quantity of catalyst. Another important feature of this method is that the catalyst can be easily recovered from the reaction mixture and reused with no loss of its catalytic activity. Copyright © 2015 John Wiley & Sons, Ltd.

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Keywords: magnetic nanoparticles; C-C coupling; biphenyl; heterogeneous catalysis

#### Introduction

Conventionally, heterogeneous catalysis is favoured over homogeneous catalysis because the former has more advantages, such as the simplicity in recovery and regeneration.<sup>[1–8]</sup> Despite their easy synthesis, heterogeneous catalysts often suffer from lower efficiency than their homogeneous counterparts.<sup>[9]</sup> Nowadays, metal nanoparticles are highly attractive tools for catalysis because of their high surface-area-to-volume ratio.<sup>[10]</sup>

According to green chemistry principles,<sup>[11]</sup> a 'green' catalyst is one that can be simply removed from the reaction mixture and reused. In this field, magnetic nanoparticles (MNPs) have been the focus of great attention as magnetically separable matrices for catalysts.<sup>[12]</sup> Several approaches for the preparation of palladium catalysts on a magnetically retrievable phase have been used. Chemical adsorption of palladium salts on MNP surfaces with subsequent reduction and formation of palladium nanoparticles is one of them.<sup>[13,14]</sup>

These nanoparticles, because of their high surface area and unique magnetic properties, have a broad range of potential uses in disciplines including physics, biomedicine, biotechnology and materials science and in catalysis support applications.<sup>[15–19]</sup> In this regard, MNP-supported catalysts have been efficiently employed as heterogeneous catalysts. The main advantage of a catalytic system based on MNPs is that the nanoparticles can be efficiently isolated from the reaction mixture through a simple magnetic separation process after completion of the reaction.<sup>[20]</sup>

Over the past few decades, the Suzuki–Miyaura and Stille reactions have emerged as powerful carbon–carbon bond forming methodologies.<sup>[21]</sup> The traditional Suzuki reaction usually proceeds using phosphine-based palladium catalysts, and there has been considerable recent interest in the development of new catalysts that are environmentally benign and efficient. Some significant advances have been made, including the use of water-soluble phosphines as ligands,<sup>[22]</sup> microwave technology,<sup>[23]</sup> nucleophilic carbene ligands,<sup>[24]</sup> ionic liquids<sup>[25]</sup> and so on.<sup>[26]</sup> The Suzuki reaction has continued to garner attention because of the many applications that result from its tolerance towards a wide range of functional groups and because of the stability, low toxicity and commercial availability of boronic acid and boronate ester reactants. The Suzuki reaction has been used on an industrial scale for the synthesis of the sartan family of hypertensive drugs and the fungicide boscalid.<sup>[27,28]</sup> Various modifications, such as new catalysts, new ligands and even ligand-free conditions, have been developed during the past two decades to render the Suzuki reaction simple, mild and efficient.<sup>[29]</sup>

As a part of our continuing interest in the development of efficient and new heterogeneous catalysts for organic synthesis,  $^{[30-33]}$  herein we report a recoverable and efficient MNP-supported Pd (Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd) complex, which exhibits a high catalytic activity in the Suzuki and Stille cross-coupling reactions. In addition, the catalyst can be easily recovered from the reaction mixture by simple filtration and reused at least five times without significant loss of its catalytic activity.

#### Experimental

#### Materials and instrumentation

Chemicals were purchased from Fisher and Merck. The reagents and solvents used in this work were obtained from Sigma-Aldrich, Fluka or Merck and utilized without further purification.

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Department of Chemistry, Faculty of Science, Ilam University, PO Box 69315516, Ilam, Iran The particle morphology was examined using SEM with a FESEM-TESCAN MIRA3. Thermogravimetric analysis (TGA) curves were recorded using a PL-STA 1500 device (Thermal Sciences). The particle size and morphology were investigated using a Zeiss-EM10C transmission electron microscopy (TEM) instrument at an accelerating voltage of 80 kV. Vibrating sample magnetometry measurements were performed using an MDKFD magnetometer. The magnetization measurements were carried out in an external field up to 15 kOe at several temperatures. Fourier transform infrared (FT-IR) spectroscopic analyses were carried out with a Vertex 70 FT-IR spectrophotometer (Bruker, Germany) in the range 400–4000 cm<sup>-1</sup>. The amount of Pd in the catalyst was measured using an inductively coupled plasma atomic emission spectrometer (Sare Kelasam, PerkinElmer, Optima 8000).

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

A mixture of FeCl<sub>3</sub>·6H<sub>2</sub>O (5.838 g, 0.022 mol) and FeCl<sub>2</sub>·4H<sub>2</sub>O (2.147 g, 0.011 mol) was dissolved in 100 ml of deionized water in a three-necked round-bottom flask (250 ml) at 80 °C under nitrogen atmosphere. Subsequently, 10 ml of aqueous NH<sub>3</sub> solution (32%) was added to the mixture within 30 min with vigorous mechanical stirring. The black precipitate obtained was isolated by magnetic decantation, washed with double-distilled water until neutrality, and further washed twice with ethanol and dried at 80 °C in vacuum.

#### Preparation of Fe<sub>3</sub>O<sub>4</sub>-(3-aminopropyl)triethoxysilane

The obtained MNP powder (1.5 g) was dispersed in a mixture of ethanol and water (250 ml, 1:1 by volume) using sonication for 30 min. Then, (3-aminopropyl)triethoxysilane (99%, 3 ml) was added to the mixture with mechanical stirring under nitrogen atmosphere at room temperature for 8 h. The resulting product was redispersed in ethanol using sonication. The final product was washed with copious amounts of deionized water and ethanol, magnetically decanted and dried under vacuum at room temperature overnight.

#### Preparation of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP

The amino-functionalized MNPs (1 g) were dispersed in dry  $CH_2CI_2$  (3 ml) in an ultrasonic bath for 10 min, and the flask was cooled in an ice–water bath. Triethylamine (3.2 ml) was added and stirred for 30 min. Subsequently, acryloyl chloride (0.8 ml, 9.84 mmol) was added dropwise over a period of 30 min at room temperature. The mixture was stirred at room temperature for 48 h. Then, the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP nanoparticles were separated by magnetic decantation and washed three times with acetone and deionized water to remove the unattached substrates. The resulting material was dispersed in methanol (10.0 ml), stirred with piperazine (2.0 mmol, 0.172) and then stirred for a week at room temperature. The solids were separated using a magnetic field and washed with acetone. The resulting product was dried under vacuum for 12 h.

#### Preparation of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd nanocatalyst

The Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP (0.5 g) was added to a round-bottom flask containing a solution of Pd(OAc)<sub>2</sub> (0.25 g) in ethanol (20 ml). The mixture was then stirred vigorously at reflux conditions for 20 h. The solid was separated by magnetic decantation. The magnetic catalyst was washed with copious amounts of ethanol and dried under vacuum at room temperature.

#### General procedure for Suzuki reaction

To a stirred solution of aryl halide (1 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.424 g, 3 mmol) and sodium tetraphenylborate (0.5 mmol) or phenylboronic acid (1 mmol) in poly(ethylene glycol) (PEG; 2 ml) was added Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd (4 mg), and the reaction mixture was stirred at 80 °C. Completion of the reaction was determined using TLC. After cooling the reaction mixture, the catalyst was separated using an external magnet and reused in the next experiment. The mixture was diluted with diethyl ether and water and the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> (1.5 g). Finally the solvent was evaporated and corresponding biphenyl was obtained in 40–98% yield.

#### General procedure for stille reaction

To a stirred solution of aryl halide (1 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.424 g, 3 mmol) and triphenyltin chloride (0.5 mmol) in PEG (2 mm) was added Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd (4 mg), and the reaction mixture was stirred at 80 °C. Completion of the reaction was determined using TLC. The reaction mixture was then cooled down and the catalyst was separated using an external magnet and reused as such for the next run. The mixture was diluted with diethyl ether and water and the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> (1.5 g). Finally the solvent was evaporated and corresponding biphenyl product was obtained.

### **Results and discussion**

#### Characterization of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd

In order to immobilize the palladium complex, (3-aminopropyl) triethoxysilane was first loaded on the surface of nanoparticles via coordination bonding through hydroxyl group interaction, to achieve amino-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Then, the reaction of amino groups with acryloyl chloride led to acryloxyl group-functionalized Fe<sub>3</sub>O<sub>4</sub> MNPs. The Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP nanocatalyst was prepared by the Michael reaction of the acryloxyl groups with piperazine. Ultimately, Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd nanocatalyst was prepared by reaction of Pd(OAc)<sub>2</sub> with the resulting ligand (MNP-PAP) in ethanol. Piperazine was chosen as a ligand for chelating palladium due to the fact that Pd–N bonding interactions are stable



Scheme 1. Synthesis of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd.

and inert towards cleavage. Scheme 1 illustrates the detailed synthetic procedure for  $Fe_3O_4/SiO_2$ -PAP-Pd nanoparticles.

The surface morphology of the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd nanocatalyst was characterized through SEM and TEM. SEM images of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd (Figs. 1(a) and (b)) exhibit a cluster of aggregated spherical particles with an average size of 5–20 nm. Energy dispersive X-ray spectroscopy (EDS) analysis provides local information of various elements. EDS analysis of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd (Fig. 1(c)) shows that the distribution of elements (atomic percent) in the





Figure 1. (a, b) SEM images of  $Fe_3O_4/SiO_2\text{-PAP-Pd}$  at different magnifications. (c) EDS analysis.

surface of the nanosolid is C = 19.61%, Fe = 57.00%, O = 15.02% and Pd = 4.92%. The exact amount of palladium in Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd was measured using inductively coupled plasma atomic emission spectroscopy, and is found to be  $1.9 \times 10^{-3}$  mol g<sup>-1</sup>.

Interpretations made on the basis of SEM images are further supported by the TEM images shown in Figs. 2(a) and (b). The mean diameter of  $Fe_3O_4/SiO_2$ -PAP-Pd is found to be around 5–20 nm. Analysis of the TEM images shown in Figs. 2(a) and (b) indicates that the diameter of each particle species is  $11.59 \pm 2$  nm and  $20.0 \pm 1.8$  nm. The surface morphology of supported  $Fe_3O_4/SiO_2$ -PAP-Pd displays spherical particles, which are surrounded by rather uniform organic layers (Fig. 2(a)).

Dynamic laser scattering measurements of  $Fe_3O_4/SiO_2$ -PAP-Pd are shown in Figs. 2(c) and (d). The hydrodynamic diameter of the nanoparticles in water is found to be monodisperse with a mean value of 25.5 nm. Also, agglomeration of  $Fe_3O_4/SiO_2$ -PAP-Pd due to the van der Waals force between the particles reduces after surface modification.

The magnetic properties of Fe<sub>3</sub>O<sub>4</sub> and the catalyst were determined using vibrating sample magnetometry (Fig. 3), which shows that the Fe<sub>3</sub>O<sub>4</sub> MNPs are ferromagnetic with a saturation magnetization of 78 emu g<sup>-1</sup>, while the saturation magnetization of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd is 37.6 emu g<sup>-1</sup>. The slight decrease observed in the saturation magnetization of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd is due to the successful grafting of SiO<sub>2</sub>-PAP-Pd on the surface of Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub> MNPs, amino-functionalized MNPs, MNP– acryloxyl and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd are shown in Fig. 4. In Fig. 4(a), the characteristic peaks around 580 and 3000–3500 cm<sup>-1</sup> can be assigned to Fe–O and O–H stretching bonds, respectively. In the spectrum of amino-functionalized MNPs (Fig. 4(b)), bands corresponding to Si–O stretching appear at 1011 and 1001 cm<sup>-1</sup>. Furthermore, characteristic peaks of C–H aliphatic bond are observed at 2854–2922 cm<sup>-1</sup>, and also a broad band appears at 3394 cm<sup>-1</sup>, which is related to the stretching vibration of NH<sub>2</sub> groups. In the spectrum of Fe<sub>3</sub>O<sub>4</sub>–acryloxyl (Fig. 4(c)), absorption bands at 1710 and 1642 cm<sup>-1</sup> are attributed to C=O and C=C bonds and the peak



**Figure 2.** TEM images of  $Fe_3O_4/SiO_2$ -PAP-Pd at (a) × 63 000 and (b) × 100 000 magnification. (c, d) Dynamic laser scattering measurements.

observed at  $3020 \text{ cm}^{-1}$  corresponds to the secondary amide group. The peaks at 1245 and 1164 cm<sup>-1</sup> can be assigned to C–N and C–O stretching of ether groups, respectively. In the FT-IR spectrum of



Figure 3. Magnetization curves for (a)  $Fe_3O_4$  and (b)  $Fe_3O_4$ /SiO<sub>2</sub>-PAP-Pd.



Figure 4. FT-IR spectra of (a)  $Fe_3O_4$  MNPs, (b) amino-functionalized MNPs, (c) MNP–acryloxyl and (d)  $Fe_3O_4/SiO_2$ -PAP-Pd.

Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd (Fig. 4(d)), there are some peaks that are shifted and some have disappeared and new peaks are observed. Significant decreases of bands of functional groups on Fe<sub>3</sub>O<sub>4</sub>/ SiO<sub>2</sub>-PAP-Pd are detected at 1701 and 1155 cm<sup>-1</sup>, which correspond to C=O and -C-C- stretching, respectively.

Figure 5 shows the thermal analysis of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>/ SiO<sub>2</sub>-PAP-Pd nanoparticles. In the TGA curve of Fe<sub>3</sub>O<sub>4</sub>, weight loss is mainly divided into two regions: below 200 °C and 200–600 °C. Weight loss of about 3% below 200 °C is assigned to the loss of physically adsorbed water and surface hydroxyl groups. The weight loss of about 8% between 260 and 600 °C may be associated with the thermal crystal phase transformation from Fe<sub>3</sub>O<sub>4</sub> to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.<sup>[33]</sup>

Differential thermal analysis (DTA; Fig. 5) shows an endothermic peak at below 200 °C. The endothermic effect below 200 °C may be due to removal of physically absorbed water and the endothermic effect at 246 °C is due to removal of structurally absorbed water. The exothermic peak between 260 and 600 °C is due to recrystallization and phase transformation from Fe<sub>3</sub>O<sub>4</sub> to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

There are two weight loss steps in the TGA curve of  $Fe_3O_4/SiO_2$ -PAP-Pd (Fig. 5(b)). A small amount of loosely bound hydroxyl and water causes the weight loss (less than 4.9%) below 200 °C. This is followed by a weight loss of about 14.1% between 200 and 425 °C that is due to decomposition of organic moieties of the complex.



Figure 5. TGA/DTA curves of (a)  $Fe_3O_4$  and (b)  $Fe_3O_4$ /SiO<sub>2</sub>-PAP-Pd.

#### **Catalytic studies**

The catalytic activity of  $Fe_3O_4/SiO_2$ -PAP-Pd was evaluated in the C–C coupling reaction of aryl halides with tetraphenylborate, phenylboronic acid and triphenyltin chloride.

In our preliminary experiments, the reaction between 1bromo-4-nitrobenzene and sodium tetraphenylborate was investigated to optimize the reaction conditions, including catalyst amount, base, solvent and temperature. The results are summarized in Table 1.

Initially, the solvent effect was examined, and a significant solvent effect is observed. We find that the nature of solvent significantly affects the conversion of the coupling reaction. Among the tested solvents, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) lead to corresponding biphenyl product in  $57\pm9$  and  $59 \pm 7\%$  yields (Table 1, entries 1 and 2) in the presence of 4 mg of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd. While in solvents such as water and EtOH, trace amounts of product are obtained (Table 1, entries 3 and 4) and in 1,4-dioxane no product is observed (Table 1, entry 5). In the case of PEG-400 solvent the product is isolated in  $98 \pm 2\%$ yield (Table 1, entry 6). Consequently, PEG-400 was finally selected as the best solvent for the coupling reaction based on product yield.Our next studies focused on the effect of base in the model reaction, with various bases (NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, KOH, NaOH, N,Ndimethylpyridin-4-amine (DMAP) and Et<sub>3</sub>N) being examined. The reaction does not occur in the absence of base (Table 1, entry 12) and the presence of base has a significant effect in the Suzuki coupling reaction. Among the examined bases, it is found that

Table 1. C-C coupling of 1-bromo-4-nitrobenzene with sodium tetraphenylborate in the presence of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd under various conditions<sup>a</sup> NaPh₄B Temperature Catalyst Yield Entry Solvent Base Time (%)<sup>b</sup> (mmol) (°C) (mq)(min) 1 DMF Na<sub>2</sub>CO<sub>3</sub> 80 4 35  $57 \pm 9$ 2 DMSO Na<sub>2</sub>CO<sub>3</sub> 80 4 35  $59 \pm 7$ 3 Na<sub>2</sub>CO<sub>3</sub> 35  $H_2O$ 80 4 Trace 4 **EtOH** Na<sub>2</sub>CO<sub>3</sub> Reflux 4 35 Trace 5 1,4-Dioxane Na<sub>2</sub>CO<sub>3</sub> 80 4 35 6 PEG Na<sub>2</sub>CO<sub>3</sub> 4 35 98±2 80 7 PFG 4 Et<sub>3</sub>N 80 35 Trace 8 PEG DMAP 80 4 35 Trace 9 PEG KOH 80 35  $60 \pm 3$ 4 10 PFG NaOH 80 4 35 40 + 611 PEG NaHCO<sub>3</sub> 80 4 35  $74 \pm 11$ 12 PEG 80 300 4 \_ 13 PEG  $Na_2CO_3$ Room temp. 4 240 14 PEG 4 240  $25 \pm 6$ Na<sub>2</sub>CO<sub>3</sub> 50 15 PEG Na<sub>2</sub>CO<sub>3</sub> 4 35  $98 \pm 2$ 80 PEG 16 Na<sub>2</sub>CO<sub>3</sub> 100 4 35 98 + 217 PEG 3 72±8 Na<sub>2</sub>CO<sub>3</sub> 80 150 18 PEG Na<sub>2</sub>CO<sub>3</sub> 80 5 35  $98 \pm 1$ 19 PEG Na<sub>2</sub>CO<sub>3</sub> 80 1440

<sup>a</sup>Reaction conditions: 1-bromo-4-nitrobenzene (1 mmol), NaPh<sub>4</sub>B (0.5 mmol), base (3 mmol), solvent (2 ml). <sup>b</sup>Isolated vield. Na<sub>2</sub>CO<sub>3</sub> acts as an excellent base for this reaction (Table 1, entry 6). Organic bases such as Et<sub>3</sub>N and DMAP are substantially less effective (Table 1, entries 7 and 8). In the presence of other bases, KOH, NaOH and NaHCO<sub>3</sub>, low to moderate yields are obtained (Table 1, entries 9-11). As mentioned above, the Suzuki cross-coupling reaction is considered in the presence of different bases including monobasic (KOH, NaOH), dibasic (Na<sub>2</sub>CO<sub>3</sub>) and organic basic materials. The biggest difference between the monobasic (KOH, NaOH) and the bibasic (Na<sub>2</sub>CO<sub>3</sub>) bases is that KOH and NaOH are the stronger bases, while  $Na_2CO_3$  and  $NaHCO_3$  are weak bases, based on their known  $K_b$ values. As previously reported by Knecht and co-workers,<sup>[34]</sup> for KOH or NaOH, the amount of free and reactive hydroxide is higher as compared to the Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> systems, which results in a strong combination with palladium species leading to a decrease in biphenyl yield. Also, organic bases such as Et<sub>3</sub>N and DMAP are not strong enough for this cross-coupling reaction. Based on these results we find that a moderate base capacity is necessary to perform the coupling reaction in the presence of a catalytic amount of  $Fe_3O_d/$ SiO<sub>2</sub>-PAP-Pd. Therefore, when Na<sub>2</sub>CO<sub>3</sub> and HNaCO<sub>3</sub> are considered, a different trend in reactivity is observed, with higher product yields as compared to KOH, NaOH or organic bases. Based on this study, Na<sub>2</sub>CO<sub>3</sub> was finally selected as the best base for this reaction.

This reaction is sensitive to temperature. Therefore the effect of temperature on the outcome of the reaction was investigated. It is found that higher temperatures can improve the reaction rate and shorten the reaction time (Table 1, entries 13–16). Further studies reveal that the optimal reaction temperature is  $80 \,^{\circ}$ C (Table 1, entry 15).

The effect of the amount of sodium tetraphenylborate on the yield was also investigated (Fig. 6). Reactions carried out in the presence of 0.2, 0.3, 0.4 and 0.5 mmol of sodium tetraphenylborate afford isolated yields of  $52\pm9$ ,  $74\pm7$ ,  $83\pm3$  and  $98\pm2\%$ , respectively. It is found that 0.5 mmol of sodium tetraphenylborate with 1 mmol of 1-bromo-4-nitrobenzene are the appropriate amounts for the completion of the reaction.

Since the coupling reaction does not occur in the absence of catalyst (Table 1, entry 19), the amount of palladium catalyst was evaluated. It is found that 4 mg of  $Fe_3O_4/SiO_2$ -PAP-Pd is the optimal amount, while when the amount of catalyst is decreased, lower yield is achieved (Table 1, entry 17). Increasing the amount of



Figure 6. Effect of amount of sodium tetraphenylborate on outcome of reaction.

<b>Table 2.</b> Pd <sup>a</sup>	Suzuki-type C–C coupling rea	action of aryl hal	ides with sodium to	etraphenylborate	e in the presence of	catalytic amounts of Fe	<sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> -PAP-
		X R +	NaPh <sub>4</sub> B <u>Fe<sub>3</sub>O<sub>4</sub>/SiC</u> Na <sub>2</sub> CO	D <sub>2</sub> -PAP-Pd ►			
Entry	R	Х	Time (min)	Yield (%) <sup>b</sup>	M.p. (°C)		TOF
					Found	Reported	(h <sup>-'</sup> ) <sup>c</sup>
1	Н	I	20	98	67–68	68-70 <sup>[26]</sup>	3722
2	2-CO <sub>2</sub> H	I	60	92	107-109	111–113 <sup>[35]</sup>	1165
3	4-CH <sub>3</sub>	I	30	95	44–47	44-46 <sup>[26]</sup>	2405
4	4-OCH <sub>3</sub>	I	20	97	84–85	88-90 <sup>[26]</sup>	3932
5	4-CH <sub>3</sub>	Br	15	96	44–47	44-46 <sup>[26]</sup>	5189
6	Н	Br	35	92	67–68	68-70 <sup>[26]</sup>	2084
7	4-CN	Br	37	97	82-83	85-86 <sup>[29]</sup>	2126
8	4-CHO	Br	45	96	56–58	54-56 <sup>[28]</sup>	1730
9	4-OH	Br	20	95	162–163	163–164 <sup>[29]</sup>	3851
10	4-SH	Br	25	93	105–106	110-111 <sup>[36]</sup>	3016
11	4-NO <sub>2</sub>	Br	35	98	113–115	112–114 <sup>[26]</sup>	2270
12	4-NH <sub>2</sub>	Br	30	95	52–54	50-53 <sup>[28]</sup>	2568
13	4-CO <sub>2</sub> H	Br	100	89	219-223	224-228 <sup>[35]</sup>	722
14	2-CH <sub>2</sub> OH	Br	70	98	Oil	Oil <sup>[37]</sup>	1135
15	3-CHO	Br	60	86	46-48	53–54 <sup>[38]</sup>	1162
16	2-Br-naphthalene	Br	1440	60	Oil	Oil <sup>[29]</sup>	34
17	4-CHO	Cl	1200	40	57–58	54-56 <sup>[28]</sup>	27
18	4-CO <sub>2</sub> H	Cl	1440	52	219–223	224–228 <sup>[39]</sup>	29
<sup>a</sup> Reaction	conditions: arvl halide (1 mm	ol), NaPh₄B (0.5	mmol), base (3 mm	ol), Fe₃O₄/SiOっ-P	AP-Pd (4 mg), PEG-40	00 (3 ml).	

<sup>a</sup>Reaction conditions: aryl halide (1 mmol), NaPh<sub>4</sub>B (0.5 mmol), base (3 mmol), Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd (4 mg), PEG-400 (3 ml). <sup>b</sup>Isolated yield.

<sup>c</sup>Turnover frequency.

Table 3. Suzuki-type C–C coupling reaction of aryl halides with phenylboronic acid in the presence of catalytic amounts of Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> -PAP-Pd <sup>a</sup>								
$\frac{X}{R} + PhB(OH)_2 \frac{Fe_3O_4/SiO_2-PAP-Pd}{Na_2CO_3, PEG} R$								
Entry	R	Х	Time (min)	Yield (%) <sup>b</sup>	M.p. (°C)		TOF	
					Found	Reported	(h ') <sup>c</sup>	
1	Н	I	8	98	67–68	68-70 <sup>[26]</sup>	9932	
2	2-CO₂H	I	25	94	107-109	111–113 <sup>[35]</sup>	3049	
3	4-CH₃	I	15	97	44–47	44-46 <sup>[26]</sup>	5243	
4	4-OCH₃	I	10	93	84–85	88-90 <sup>[26]</sup>	7540	
5	4-CH₃	Br	12	99	44–47	44-46 <sup>[26]</sup>	6689	
6	Н	Br	17	93	67–68	68–70 <sup>[26]</sup>	4436	
7	4-CN	Br	40	99	82-83	85-86 <sup>[29]</sup>	2006	
8	4-CHO	Br	30	98	56–58	54-56 <sup>[28]</sup>	2649	
9	4-OH	Br	15	98	162–163	163–164 <sup>[29]</sup>	5297	
10	4-SH	Br	25	70	105-106	110–111 <sup>[36]</sup>	2270	
11	4-NO <sub>2</sub>	Br	14	97	113–115	112–114 <sup>[26]</sup>	5618	
12	4-NH <sub>2</sub>	Br	18	97	52–54	50-53 <sup>[28]</sup>	4369	
13	4-CO₂H	Br	50	90	219–223	224–228 <sup>[39]</sup>	1459	
14	3-CHO	Br	35	95	46–48	53–54 <sup>[38]</sup>	2201	
15	2-Br-naphthalene	Br	1440	96	Oil	Oil <sup>[29]</sup>	54	
16	4-CHO	Cl	1440	83	57–58	54–56 <sup>[28]</sup>	47	
30			N I (2					

<sup>a</sup>Reaction conditions: aryl halide (1 mmol), PhB(OH) (1 mmol), base (3 mmol), Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd (4 mg), PEG-400 (3 ml). <sup>b</sup>Isolated yield.

<sup>c</sup>Turnover frequency.

triphenyltin chloride in the presence of catalytic amounts of Fe $_3O_4/SiO_2\text{-PAP-Pd}^a$								
$ \begin{array}{c} X \\ Fe_3O_4/SiO_2-PAP-Pd \\ R \\ R \end{array} $								
Entry	r R	Х	Time	Yield	M.p. (°C)		TOF	
			(min)	(%)	Found	Reported	(n ) <sup>-</sup>	
1	н	Ι	20	95	67–68	68-70 <sup>[26]</sup>	3851	
2	4-CH <sub>3</sub>	I	120	96	44–47	44-46 <sup>[26]</sup>	649	
3	$4-OCH_3$	I	60	40	84–85	88-90 <sup>[26]</sup>	540	
4	$4-CH_3$	Br	60	93	44–47	44-46 <sup>[26]</sup>	1257	
5	Н	Br	35	94	67–68	68–70 <sup>[26]</sup>	2178	
6	4-CN	Br	50	98	82–83	85-86 <sup>[29]</sup>	1589	
7	4-CHO	Br	180	91	56-58	54–56 <sup>[28]</sup>	410	
8	4-Cl	Br	55	89	70–71	77–79 <sup>[26]</sup>	1312	
9	4-OH	Br	50	95	162–163	163–164 <sup>[29]</sup>	1540	
10	Н	Cl	240	51	70–71	68-70 <sup>[26]</sup>	172	

Table 4. Stille-type C–C coupling reaction of anyl halides with

<sup>a</sup>Reaction conditions: aryl halide (1 mmol), Ph<sub>3</sub>SnCl (0.5 mmol), base (3 mmol), Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd (4 mg), PEG-400 (3 ml).

<sup>b</sup>lsolated yield.

<sup>c</sup>Turnover frequency.



Figure 7. Recyclability of catalyst for preparation of 4-nitro-1,1'-biphenyl.

 $Fe_3O_4/SiO_2$ -PAP-Pd catalyst to 5 mg does not effectively increase the yield of product (Table 1, entry 18).

To explore the generality and scope of the catalytic system under investigation, coupling of various aryl halides with sodium tetraphenylborate was examined. The results are summarized in Table 2. In general, all of the reactions proceed smoothly to afford the corresponding biphenyl products in good to excellent yields. The electronic nature of the substituents does not seem to affect the reaction rates or product yields. Also, the reactions of aryl chlorides with substituted groups such as  $-CO_2H$  and -CHO on the benzene rings with sodium tetraphenylborate afford the corresponding products. Reaction of aryl chloride with sodium tetraphenylborate needs 8 mg of  $Fe_3O_4/SiO_2$ -PAP-Pd and a temperature of 100 °C (Table 2, entries 17 and 18).

To extend the scope of our work, we next investigated the coupling of various aryl halides with phenylboronic acid. The reactions of halobenzenes with phenylboronic acid (1 mmol) in the presence of 4 mg of catalyst in PEG-400 (2 ml) as solvent were studied. The results are summarized in Table 3. The Suzuki cross-coupling reactions of phenylboronic acid with aryl iodides bearing electrondonating or electron-withdrawing groups at their *meta*-positions or *ortho*-positions all give the corresponding biphenyl in high yields.

The Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>-PAP-Pd catalyst also shows a high activity for the Stille reaction in PEG solvent using organostannane (Ph<sub>3</sub>SnCl, 0.5 mmol). As evident from Table 4, the results are similar to those for the Suzuki reaction. Aryl iodides and aryl bromides give better results than aryl chlorides.

For practical purposes, easy recyclability of a catalyst is highly desirable. To investigate this issue, the recyclability of the catalyst was examined for the reaction of 1-bromo-4-nitrobenzene and sodium tetraphenylborate. We find that this catalyst demonstrates excellent reusability. After completion of the reaction, the catalyst is easily and rapidly separated from the reaction mixture using an external magnet and decantation of the reaction solution. The remaining magnetic nanocatalyst was washed with ethyl acetate to remove residual product. Then, the reaction vessel was charged with fresh substrate and subjected to the next run. As shown in Fig. 7, the catalyst can be recycled for up to five runs without any significant loss of its catalytic activity.

#### Conclusions

In summary, we have successfully developed a novel, efficient and practical method for the synthesis of biphenyl derivatives through the reaction of aryl halides with sodium tetraphenylborate, phenylboronic acid or triphenyltin chloride using  $Fe_3O_4/SiO_2$ -PAP-Pd as catalyst under mild reaction conditions.

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