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Green and Efficient Procedure for Suzuki-Miyaura and Mizoroki-Heck Coupling Reactions Using Palladium Catalyst Supported on Phosphine Functionalized ZrO<sub>2</sub> NPs (ZrO<sub>2</sub>@ECP-Pd) as a New Reusable Nanocatalyst

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# Green and efficient procedure for Suzuki-Miyaura and Mizoroki-Heck coupling reactions using palladium catalyst supported on phosphine functionalized ZrO<sub>2</sub> NPs (ZrO<sub>2</sub>@ECP-Pd) as a new reusable nanocatalyst

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### Abstract

In this article, palladium supported on phosphine functionalized ZrO<sub>2</sub> NPs (ZrO<sub>2</sub>@ECP-Pd) has been introduced as a novel and efficient nanocatalyst for Suzuki-Miyaura and Mizoroki-Heck reactions. This new catalyst was prepared from the reaction of Pd(OAc)<sub>2</sub> and PPh<sub>2</sub>-functionalized ZrO<sub>2</sub> NPs, and then characterized using FT-IR, XRD, SEM, TEM, TGA and ICP techniques. The above-experimental results showed that the synthesized catalyst existed as spheres with a mean size range of 10-40 nm. The prepared ZrO2@ECP-Pd nanocatalyst was shown to be highly efficient in the Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions of a wide range of aryl halides including electron-rich and electron-poor aryl iodides/bromides, and heteroaryl iodides, affording the corresponding products in good to excellent yields in short reaction times. The notable feature of the present protocol is that use of water and [bmim]PF<sub>6</sub> as environmentally benign solvents, which eliminate the need of toxic solvent. In addition to the aforementioned favorable properties, the nanocatalyst can be recovered and reused for the subsequent reactions (at least six times) without any appreciable loss of efficiency.

#### 1. Introduction

Formation of carbon-carbon bond is one of the most essential transformations in synthetic chemistry and industrial processes.<sup>1-4</sup> In this regard, many transition metals have been recognized as powerful and versatile catalysts for this reaction. <sup>5,6</sup> In this among, palladium, which is one of the valuable transition metal, is widely employed as an efficient catalyst for the cross-coupling reactions such as the Mizoroki-Heck and Suzuki-Miyaura reactions. Up to now, various palladium catalytic systems have been developed for these couplings including homogeneous and heterogeneous catalysts.7-10 Although, homogeneous palladium catalyst provides excellent activity and selectivity but suffer from the problems such as separating the catalyst from the reaction mixture, catalyst recycling and the contamination of the ligand residue in the final products.<sup>11</sup> Considering these facts, there are numerous efforts on the heterogenization of palladium complexes on different supports, which is a promising way to solve some of the technical application problems associated with homogeneous system. 12-20 The key features of the heterogeneous Pd complex including easy separation and facile recycling catalyst. However, one of the great drawbacks of such catalysis is that the resulting immobilized catalysts often display much lower catalytic efficiency than their homogeneous counterparts. Therefore, in the last years many different studies have been performed looking for obtaining better catalytic activity for this type of catalyst. <sup>21-22</sup>

In this term, nanoparticles have recently generated a new research line which can be used as alternative surface for supporting homogeneous catalysts. Because of their large surface area, nanoparticles have higher catalyst loading capacity and higher dispersion than many conventional support matrixes, leading to dramatic enhancements in the catalytic activity of the supported catalysts.<sup>23-28</sup> To date, many nanoparticles have been explored to be candidates for immobilization of Pd complexes such as carbon nanotubes,<sup>29</sup> nanoSiO<sub>2</sub>,<sup>30</sup> graphene nanosheets (GNS),<sup>31-32</sup> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles.<sup>33-34</sup> In this area, zirconia nanoparticles (ZrO<sub>2</sub> NPs) have received a great deal of attention because of their superior chemical, thermal and mechanical properties in a wide range of applications such as catalysts, oxygen sensors, fuel cells, engine parts and thermal barrier coatings on metal surfaces. Moreover, recent studies show that ZrO<sub>2</sub> NPs have emerged as promising supports for immobilization metal nanoparticles.

In addition, during the past decades, a great deal of attention has been paid to developing greener chemical processes and synthetic methods. To date, the reported coupling reactions were mostly carried out in organic solvents which are a major cause of ecological contamination.<sup>39</sup> In order to comply with the idea of green chemistry, one approach is to utilize water, which is non-toxic, cheap and inflammable instead of toxic and expensive organic solvent.<sup>40</sup> However, several examples of palladium catalyzed coupling reactions in aqueous media have been reported, but many substrates of these reactions have poor solubility in water, and solubility is generally considered as a prerequisite for reactivity. A way to overcome this difficulty would be the use of ionic liquids (ILs), which are known as ecofriendly, reusable and alternative reaction media in organic synthesis. Among the various solvents, ILs show several advantages which make them more attractive and ecologically acceptable such as non-volatility, wide liquid range, high thermal stability, low toxicity, good solubility, reusability, and incombustibility. 41

Based on this background, and in continuation of our efforts in designing novel and efficient heterogeneous catalysts, 42-51 herein, we would like to report synthesis and characterization of a novel palladium catalyst supported on phosphine functionalized ZrO<sub>2</sub> NPs and its application in the Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions. According to the urgent need for more environmentally responsible chemistry, green solvents such as water and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF<sub>6</sub>) were employed instead of the most commonly used toxic solvents in Suzuki-Miyaura and Mizoroki-Heck reactions, respectively. Results showed that the new catalyst can provide excellent reactivity in the coupling reactions under environmentally friendly conditions (Scheme 1).



Scheme 1 Preparation steps of ZrO<sub>2</sub>@ECP-Pd nanocatalyst.

# 2. Experimental

2.1 General. The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FTIR spectra were recorded on pressed KBr pellets using AVATAR 370 FT-IR spectrometer (Therma Nicolet spectrometer, USA) at room temperature in the range between 4000 and 400  $cm^{-1}$  with a resolution of 4  $cm^{-1}$ . The NMR spectra were provided on Brucker Avance 300, 400 and 500 MHz instruments in DMSO-d<sub>6</sub> and CDCl<sub>3</sub>. Mass spectra were recorded with a CH7A Varianmat Bremem instrument at 70 eV electron impact ionization, in m/z (rel %). TGA analysis was performed using a Shimadzu Thermogavimetric Analyzer (TG-50) in the temperature range of 25-800 °C at a heating rate of 10 °C /min under air atmosphere. SEM images were recorded using Leo 1450 VP (LEO, Germany) scanning electron microscope operating at an acceleration voltage 20 kV, resolution of about 2 nm. Transmission electron microscopy (TEM) was performed with a Leo 912 AB microscope (Zeiss, Germany) with an accelerating voltage of 120 kV. The crystal structure of catalyst was analyzed by XRD using a D8 ADVANCE -Bruker diffractometer operated at 40 kV and 30 mA utilizing CuKa radiation ( $\lambda = 0.154$  A°). Inductively coupled plasma (ICP) analysis was carried out with a Varian VISTA-PRO, CCD (Australia). All yields refer to isolated products after purification by thin layer chromatography. In addition, all of the products were known compounds and they were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR spectroscopy, and mass spectrometry and comparison of their melting points with known compounds (see supporting information).

**2.2 Synthesis of ZrO<sub>2</sub> NPs.** To a solution of ZrOCl<sub>2</sub>8H<sub>2</sub>O (0.003 mol, 0.966 g) in 50 mL distilled water,

citric acid (0.126 mol, 24.207 g) and ethylene glycol (0.126 mol, 7.045 mL) were added at room temperature. The resulting solution was stirred at 80°C for 30 min and then refluxed for 12h until a white sol was obtained. In order to increase polymerization between citric acid, ethylene glycol and ZrOCl<sub>2</sub>.8H<sub>2</sub>O, the reaction mixture was cooled down and then slowly heated at 80 °C for 10 h in an open bath. After that the sol became more viscous as a wet gel. Finally, the wet gel was dried by direct heating on the hot plate at 120 °C for 8 h to afford brown powder. The brown powder was calcined at 750 °C for 4h at a rate of 4 °C min to give ZrO<sub>2</sub> NPs as a white powder. <sup>52</sup>

2.3 Surface coating of ZrO<sub>2</sub> NPs by epichrorohydrin (ZrO<sub>2</sub>@EP NPs). ZrO<sub>2</sub> NPs powder (2 g) was suspended to pure epichrorohydrin (10 mL) at 60 °C with vigorous stirring. After 24 h the resulting suspension was cooled to room temperature and centrifuged. The white precipitate was washed with methanol (4×15) until removing additional amount of epichlorohydrin. The epoxy modified ZrO<sub>2</sub> NPs were then dried at 100 °C under vacuum for 8 h. <sup>42</sup>

2.4 Surface modification of  $ZrO_2@Ep$  by cyanuric acid ( $ZrO_2@Ep$ -Cy NPs). Cyanuric acid (4 g, 0.031 mol) was added portion by portion to a suspension of the synthetic  $ZrO_2@Ep$  NPs (1g) in DMF (20 mL). The mixture was stirred at 120 °C. After 12h the resulting  $ZrO_2@Ep$ -Cy product was collected by centrifuge, and washed with deionized water for three times and dried under vacuum at 50 °C for 12h.<sup>53</sup>

2.5 Synthesis of phosphine-functionalized  $ZrO_2$  NPs ( $ZrO_2@ECP$  NPs). To a magnetically stirred mixture of  $ZrO_2@Ep-Cy$  NPs (1 g),  $Et_3N$  (3 mL) in dry toluene (20 mL), 5 mL of chlorodiphenylphosphine was added drop by drop at room temperature. The above suspension was then stirred for 16 h at room temperature under the protection of  $N_2$ 

atmosphere. The final product (phosphine-functionalized ZrO<sub>2</sub>@ECP NPs), was separated by centrifuge and washed with ethanol (5×10) to remove excess chlorodiphenylphosphine and then dried at room temperature. <sup>54</sup>

2.6 Synthesis of  $ZrO_2@ECP-Pd$  nanocatalyst. ZrO<sub>2</sub>@ECP-Pd was prepared by mixing the ZrO<sub>2</sub>@ECP NPs (1 g) and Pd(OAc)<sub>2</sub> (0.34 mmol, 0.076 g) in ethanol (30 mL) and refluxed in 100 mL flask with stirring. After 12 h the mixture was cooled and the solid catalyst was separated by centrifuge from the reaction medium. Then the collected precipitate (ZrO<sub>2</sub>@ECP-Pd) was washed several times by ethanol before being dried under vacuo at 50 °C overnight. The preparation process was illustrated in Scheme 1.

**2.7 Typical procedure for the Suzuki-Miyaura reaction.** In a typical procedure, iodobenzene (1.0 mmol, 0.203 g), phenylboronic acid (1.2 mmol, 0.146 g), potassium carbonate (1.5 mmol, 0.207 g),  $ZrO_2@ECP-Pd$  nanocatalyst (0.31 mol %, 0.005 g), and water (3 mL) were allowed to react at 90 °C. Upon the completion of the reaction which monitored by TLC, the reaction mixture was cooled to room temperature and the catalyst was separated by centrifuge. The resulting solution was extracted with ethyl acetate (3 × 10 mL). The organic layers was combined, dried with sodium sulfate, and filtered. The filtrate was concentrated by vacuum and purified by thin layer chromatography using *n*-hexane/ethyl acetate (50/1) to afford the pure product (0.150 g, % 98 yield).

2.8 Typical procedure for the Mizoroki-Heck reaction. In a typical procedure, iodobenzene (1.0 mmol, 0.203 g), methyl acrylate (1.2 mmol, 0.108 mL), potassium carbonate (1.5 mmol, 0.207 g), ZrO<sub>2</sub>@ECP-Pd nanocatalyst (0.31 mol %, 0.005 g), and [bmim]PF<sub>6</sub> (1g, 3.5 mmol) were allowed to react at 100 °C. Upon the completion of the reaction which monitored by TLC, the reaction mixture was cooled to room temperature and the catalyst was separated by centrifuge. n-Hexane (5 ml) was added to the reaction mixture and extraction was done for 15 minutes with vigorous stirring.<sup>55</sup> The organic layer was combined and concentrated under reduced pressure to give the crude product. The final product was purified by thin layer chromatography using *n*-hexane/ethyl acetate (50/1) to afford the pure product (0.153)g, % 95 yield).

# 3. Results and Discussion

3.1 Characterization of catalyst. The palladium catalyst supported on phosphine functionalized ZrO<sub>2</sub> NPs as a new reusable nanocatalyst was prepared via multiple steps as shown in Scheme 1. The first step was to prepare ZrO2 NPs according to the procedure presented in the literature.<sup>52</sup> In the second step, the obtained ZrO<sub>2</sub> NPs were subsequently reacted with epichlorohydrin. The modified ZrO2 NPs were then sequential treated by cyanuric acid and chlorodiphenylphosphine to form ZrO<sub>2</sub>@ECP. Finally, Pd particles were immobilized on the  $ZrO_2@ECP$  through the reaction of  $ZrO_2@ECP$  with  $Pd(OAc)_2$ salt in ethanol under reflux condition. The synthesized nanocatalyst was well characterized for its physicochemical properties using analytical techniques such as Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and inductively coupled plasma (ICP).

The FT-IR spectrum of unmodified  $ZrO_2$  NPs (Figure 1a) shows a broad band around 3450-3200 cm<sup>-1</sup>, indicative of the presence of –OH groups on the nanoparticle surface. Also, as shown in Figure 1a, the strong absorption bands at 751 and 507 cm<sup>-1</sup> have been assigned to the stretching vibrations of the Zr–



**Figure 1.** FT-IR spectrum of (a) ZrO<sub>2</sub> NPs (b) ZrO<sub>2</sub>@Ep NPs (c) ZrO<sub>2</sub>@Ep-Cy NPs (d) ZrO<sub>2</sub>@ECP NPs (e) ZrO<sub>2</sub>@ECP-Pd nanocatalyst (f) reused ZrO<sub>2</sub>@ECP-Pd nanocatalyst.

O group in  $ZrO_2 NPs$ .<sup>36</sup> In the case of the functionalized  $ZrO_2 NPs$  by epichlorohydrin (Figure 1b), the characteristic absorption bands at 2943 and 2877 cm<sup>-1</sup> can be observed, which corresponded to the stretching vibration of  $-CH_2$  groups.<sup>42</sup> From the presence of these bands it can be inferred that the  $ZrO_2 NPs$  were modified by epoxy groups successfully.

From the FT-IR spectra presented in Figure 1c, corresponding to the modification  $ZrO_2 NPs$  with cyanuric acid, the intensities of -OH stretching frequencies (3624-3251 cm<sup>-1</sup>) were increased smoothly by reaction with cyanuric acid. Successful functionalization of the  $ZrO_2 NPs$  with cyanuric acid was also evidenced by the absorption bands at 1730, 1610 and 1580 cm<sup>-1</sup>, attributed to the C=N vibration of cyanuric acid ring.<sup>56</sup> Surface treatment of these modified nanoparticles with chlorodiphenylphosphine leads to the formation of phosphinterminated zirconium nanostructures (Figure 1d). The presence of phosphine ligand on the surface of  $ZrO_2 NPs$  can be seen by absorption band positioned at 1045 cm<sup>-1</sup>, which corresponding to the P-O stretching bond.<sup>57</sup>

However, the FT-IR spectrum of the synthesized nanocatalyst demonstrates that almost no change occurs after immobilization of palladium on the  $ZrO_2@ECP$  surface (Figure 1e), but it was clearly depicted in the XRD pattern of  $ZrO_2@ECP$ -Pd nanocatalyst.<sup>58</sup>

Unambiguous evidence of palladium particles on ZrO<sub>2</sub>@ECP is provided via X-ray powder diffraction analysis (XRD). The XRD patterns are shown in Figure 2. According to the reference JCPDS (card No. 37-1484 and 79-1771), mixture phases of monoclinic and tetragonal were observed in the ZrO<sub>2</sub> NPs and ZrO<sub>2</sub>@ECP-Pd structures.<sup>59</sup> Moreover, as can be seen from this figure, both standard patterns display the same distinctive signals in the range  $10^{\circ}$  to  $70^{\circ}$  (2 $\theta$ ), indicating that the crystalline structure of the ZrO2 NPs is essentially maintained. The only difference between the patterns of ZrO<sub>2</sub> NPs and ZrO<sub>2</sub>@ECP-Pd is two weak peaks appeared at  $2\theta$  = 40.1 and 46.5 which could be related to the palladium.<sup>60</sup> The Pd peaks of ZrO2@ECP-Pd nanoparticles agree well with the standard Pd (cubic phase) XRD spectrum (card No. 05-0681). According to the XRD pattern of ZrO2@ECP-Pd, the intensity of the new peaks attesting the presence of Pd is weak which

may be attributed to the good dispersion of Pd nanoparticles in the catalysis matrix (see TEM images (Figure 3c and 3d)). So, Pd nanoparticles cannot lead to the formation of regular crystal lattice. The obtained result from XRD analysis revealed that Pd particles have been successfully immobilized onto the surface of the modified  $ZrO_2$  NPs and the peak positions of the synthesized nanoparticles were unchanged.

To clarify the size and morphology of synthesized nanocatalyst, we used scanning electron microscopy (SEM) as well as transmission electron microscopy (TEM) techniques. The SEM images of the surface of ZrO2@ECP-Pd nanocatalyst are shown in Figure 3a and 3b. However size of the ZrO<sub>2</sub>@ECP-Pd particles are not clearly defined in the SEM images obtained in the present investigation. But it is evident from these images that the synthesized nanocatalyst is composed of similar spherical particles.<sup>38</sup> In order to further examine the morphological feature, TEM image was recorded for the ZrO<sub>2</sub>@ECP-Pd nanocatalyst. The typical TEM micrographs for the ZrO<sub>2</sub>@ECP-Pd nanocatalyst were shown in Figure 3c and 3d. The particles with nearly spherical morphology with size in the range of 10-40 nm were successfully prepared as shown in the figure. Moreover, the Pd nanoparticles were found to be highly dispersed on the surface of the ZrO<sub>2</sub>@ECP nanoparticles with the average diameter size of  $\sim 5$  nm

The successful modified  $ZrO_2$  NPs by organic ligands could also be confirmed by TGA analysis. As shown in Figure 4, the TGA thermogram of the  $ZrO_2@ECP$ -Pd nanocatalyst shows a weight loss of 5.45 % below 150 °C, which is due to the loss of the adsorbed water in the sample. Another large weight loss was observed in the temperature range of 150-650 °C (18.85 %), resulting from the decomposition of organic functional groups grafted to the zirconium surface. Additionally, the exact loading of Pd on the modified zirconium nanoparticles was determined to be  $0.62 \times 10^{-3}$  mol/g based on the inductively coupled plasma (ICP) analysis. The TGA thermogram and ICP analysis also proved the successful supporting of the Pd and organic ligands onto the catalyst surface.

3.2 Catalytic performance of the  $ZrO_2@ECP-Pd$ nanocatalyst for the Suzuki-Miyaura reaction. To evaluate the merit of application of this catalytic system in organic synthesis, we applied it in the Suzuki-Miyaura and Mizoroki-Heck cross-coupling reactions. The Suzuki-Miyaura cross-coupling, the reaction between boronic acid derivatives and aryl halides, is one of the most powerful and widely preferred reactions for synthesis of biaryls. Substituted biaryl compounds have considerable application for the synthesis of biologically active substances such as pharmaceuticals and herbicides.<sup>61-62</sup> Now in this stage, the applicability of the  $ZrO_2@ECP-Pd$  as a novel nanocatalyst was evaluated in the Suzuki-Miyaura cross-coupling reaction (Scheme 2).



Scheme 2 Suzuki-Miyaura coupling reaction in the presence of ZrO<sub>2</sub>@ECP-Pd nanocatalyst.



Figure 2. The XRD patterns of (a)  $ZrO_2$  NPs and (b)  $ZrO_2@ECP-Pd$  nanocatalyst.



Figure 3. (a and b) SEM images of  $ZrO_2@ECP-Pd$  nanocatalyst, (c and d) TEM images of  $ZrO_2@ECP-Pd$  nanocatalyst.



Figure 4. The TGA thermogram of ZrO<sub>2</sub>@ECP-Pd.

ifferent reaction conditions.								
Entry	Catalyst (mol%)	Molar ratios of Iodobenzene / Base	Base	Temperature (°C)	Time (min)	Isolated Yield (%)		
1	0.31	1:2	K <sub>2</sub> CO <sub>3</sub>	100	15	98		
2	0.15	1:2	K <sub>2</sub> CO <sub>3</sub>	100	30	94		
3	0.31	1:2	K <sub>2</sub> CO <sub>3</sub>	90	15	98		
4	0.31	1:2	K <sub>2</sub> CO <sub>3</sub>	80	25	90		
5	0.31	1:2	Na <sub>2</sub> CO <sub>3</sub>	90	15	94		

KHCO<sub>3</sub>

NaOAc

Et<sub>3</sub>N

Diisopropylethylamine

 $K_2CO_3$ 

K<sub>2</sub>CO<sub>3</sub>

90

90

90

90

90

90

Table 1 The Suzuki-Miyaura reaction of iodobenzene with phenylboronic acide in the presence of  $ZrO_2@ECP-Pd$  nanocatalyst under different reaction conditions.

For initial assessment of the reaction, we examined the Suzuki-Miyaura coupling reaction of the model substrate iodobenzene with phenylboronic acid using ZrO2@ECP-Pd nanocatalyst at 100 °C. Additionally, by considering the principles of green chemistry, we tried to carry out this reaction in water, which has economic and environmental advantages. As it can be seen in Table 1, using of 0.31 mol% (0.005 g catalyst contains 0.029 mg (0.0031 mmol) of Pd) of ZrO2@ECP-Pd nanocatalyst in water afforded excellent yield of product in short reaction time (15 min) (Table 1, entry 1). The yield of the desired product did not exceed 94 %, when the model reaction was performed using 0.15 mol % of ZrO2@ECP-Pd nanocatalyst (Table 1, entry 2). Effect of temperature on the activity of ZrO2@ECP-Pd nanocatalyst was also studied. Lowering the temperature to 90 °C was found to have no effect on the yield (98%) of cross-coupling product (Table 1, entry 3). Further reducing the temperature to 80 °C was accompanied by a considerable drop of yield by 90 % with longer reaction time (Table 1, entry 4). As it is known, base plays crucial role for the yield of the cross-coupling reaction, therefore, we examined the effect of different organic and inorganic bases on the model reaction (Table 1, entries 5-9). Slightly lower yields were obtained with the other inorganic bases such as Na<sub>2</sub>CO<sub>3</sub>, KHCO<sub>3</sub> (94 % and 93 %) (Table 1, entries 5 and 6). Meanwhile, for the reaction in the presence of organic bases, the desired product was obtained in low yield under other identical reaction conditions (Table 1, entries 7, 8, 9). Thus, from the bases screened, K<sub>2</sub>CO<sub>3</sub> was found to be the best base giving maximum yields of the desired product (Table 1, entry 3). Finally, different molar ratios of iodobenzene / K2CO3 (1 : 1.5 and 1 : 1) (Table 1, entries 10, 11) were tried and it was observed that decrease in molar ratio from 1:2 to 1:1.5 has no significant effect on the yield as well as reaction time (Table 1, entries 3, 10). But by reducing the molar ratio from 1:1.5 to 1:1, the yield of product decreased from 98 % to 70 % (Table 1, entry 11). According to the optimization results and the essential goal of green chemistry, the best result is obtained by using 1:1.5 molar ratio of iodobenzene /  $K_2CO_3$  at 90  $^{\rm o}C,$  in the presence of catalytic amount of ZrO2@ECP-Pd nanocatalyst (0.31 mol %) and H2O as a green solvent (Table 1, entry 10).

0.31

0.31

0.31

0.31

0.31

0.31

6

7

8

9

10

11

1:2

1:2

1:2

1:2

1:1.5

1:1

Under these optimum conditions, we next explored the generality and scope of the protocol using several substituted aryl halides and phenylboronic acids. The results are displayed in Table 2. As it is shown in Table 2, the catalytic

performance is excellent for a wide variety of aryl iodides, and provided the corresponding products in high yields (Table 2, entries 1-7). It is noteworthy that coupling reactions of aryl iodides with electron-donating substituents proceeded more slowly than coupling reactions of aryl iodides with electron-withdrawing substituents (compare entries 2 and 3 with 4 and 5). In addition, 1-iodo-2-methyl-4-nitrobenzene results the desired product in longer reaction time due to steric effect and electron donation of -Me substitution at ortho position (Table 2, entry 6). Heteroaryl iodide such as 2-iodothiophene was also good partner for this coupling reaction (Table 2, entry 7). To investigate the role of substituents on the phenylboronic acid, two reactions were carried out using 3-nitrophenylboronic acid and gave desired products in high yield after 20 and 30 min, respectively (Table 2, entries 8 and 9). To expand the scope of this methodology, a series of aryl bromides were employed to react with phenylboronic acid under the optimized conditions (Table 2, entries 10-16). Various functional groups including 4-Cl, 4-NO<sub>2</sub>, 4-CHO, 3-CHO, 4-CN, were well tolerated under the standard conditions, and the desired products were obtained in high yields. Also, when electron-rich aryl bromide such as 1-bromo-4-methoxybenzene was explored, the reaction proceeded more slowly with lower yield of the product (Table 2, entry 16). Moreover, aryl chloride such as chlorobenzene was chosen as the challenging substrate, however, the catalytic system was less effective, even after prolonged reaction time, which might be ascribed to the strong strength of the C-Cl bond, whose bond dissociation energy was 96 kcal/mol.

15

30

30

15

15

15

90

55

80

87

98

70

**3.3 Catalytic performance of the ZrO\_2@ECP-Pd nanocatalyst for the Mizoroki-Heck reaction.** The Mizoroki-Heck cross-coupling reaction, as a powerful synthetic tool for the formation of C-C bonds in organic synthesis, has been shown to have widespread application in the synthesis of natural products, <sup>63-64</sup> agrochemicals, <sup>65</sup> and pharmaceuticals. <sup>66</sup> This reaction usually involves the interaction of an aromatic halide with an alkene, in the presence of a palladium catalyst, to give an aryl alkene. So, encouraged by the exciting results with the Suzuki-Miyaura reactions, and to further evaluate the overall utility of the current methodology, the  $ZrO_2@ECP-Pd$  nanocatalyst was applied to the Mizoroki-Heck reaction (Scheme 3).

Table 2 Suzuki-Miyaura cross-coupling reactions of arylboronic acids and aryl halides catalyzed by ZrO<sub>2</sub>@ECP-Pd nanocatalyst.

$R \xrightarrow{P} B(OH)_2 \xrightarrow{ZrO_2 @ECP-Pd} R_1 \xrightarrow{R^2} R^2$						
					3a-1	
Entry	$\mathbb{R}^1$	$\mathbb{R}^2$	Х	Product	Time (min)	Isolated Yield (%)
1	Н	Н	Ι	3a	15	98
2	4-Cl	Н	Ι	3b	20	95
3	4-NO <sub>2</sub>	Н	Ι	3c	15	98
4	4-Me	Н	Ι	3d	20	94
5	4-OMe	Н	Ι	3e	30	90
6	$2-Me-4-NO_2$	Н	Ι	3f	30	80
7	2-Thiophene	Н	Ι	3g	30	90
8	Н	3-NO <sub>2</sub>	Ι	3h	20	90
9	4-OMe	3-NO <sub>2</sub>	Ι	3i	30	85
10	Н	Н	Br	3a	60	90
11	4-Cl	Н	Br	3b	60	92
12	4-NO <sub>2</sub>	Н	Br	3c	45	95
13	4-CHO	Н	Br	3ј	45	90
14	3-CHO	Н	Br	3k	60	90
15	4-CN	Н	Br	31	45	94
16	4-OMe	Н	Br	3e	120	75



 $R^{1=}Ph, 4\text{-}NO_2C_6H_4, 4\text{-}ClC_6H_4, 4\text{-}OMeC_6H_4, 4\text{-}MeC_6H_4, 4\text{-}CHOC_6H_4, 4\text{-}CNC_6H_4, 2\text{-}Thiophene$ 

X= I, Br

Scheme 3 Mizoroki-Heck coupling reaction in the presence of ZrO<sub>2</sub>@ECP-Pd nanocatalyst.

In order to find suitable conditions for the ZrO2@ECP-Pd Mizoroki-Heck reaction using the nanocatalyst, the reaction between iodobenzene and methyl acrylate was used as a model reaction and different conditions were investigated (Table 3). According to Table 3, when the model reaction was performed using 0.31 mol % of ZrO2@ECP-Pd nanocatalyst in DMF at 90 °C, the desired product was isolated in 90 % yield (Table 1, entry 1). In an effort to perform coupling reaction in more eco-friendly reaction media, various solvents such as CH<sub>3</sub>CN, H<sub>2</sub>O, EtOH were screened and found that these solvents are not suitable for the reaction (Table 3, entries 2-4). Based on the literature, it was established that ionic liquids are a candidate for using as green solvents for Mizoroki-Heck reactions,<sup>55, 67-68</sup> so, we tested 1-butyl-3- methylimidazolium hexafluorophosphate ([bmim]PF<sub>6</sub>) as solvent for the reaction. The result showed that the corresponding coupling product was obtained in 90 % yield, although longer reaction times were required (Table 3, entry 5). For further improvement of the reaction rate and yield, the coupling reaction was carried out using higher temperature (100 °C). Pleasingly, this resulted in excellent yield of the corresponding product within 30 min (Table 1, entry 6). As illustrated in Table 3 (entries 7 and 8), in the reactions employing K<sub>2</sub>CO<sub>3</sub>, and NaOAc as the bases, the coupling reactions did not progress efficiently. In addition, the amount of ZrO2@ECP-Pd nanocatalyst was optimized using different amounts (0.40 mol% and 0.15 mol%) of the catalyst. It was found that an increase in the amount of

catalyst did not improve the results to any great extent, whereas, applying 0.15 mol% of catalyst led to lower reaction yield (80%) (Table 3, entries 9 and 10). The overall finding, based on the results given in Table 2, is that the highest catalytic activity is achieved when the Mizoroki-Heck reaction is carried out using 0.31 mol% of  $ZrO_2@ECP-Pd$  nanocatalyst in [bmim]PF<sub>6</sub> as environmentally benign solvent at 100 °C (Table 2, entry 6).

With the optimum reaction conditions in hand, in the next step, various substituted aryl halides and olefins were examined to explore the scope and efficiency of this approach. The representative results are summarized in Table 4. Generally, all of the coupling products were obtained in good to excellent yields (70-98 %) during 20-180 min (Table 4, entries 1-20). In comparison, the coupling reactions of aryl bromides result the desired products in longer reaction times than the reactions of aryl iodides, due to the different dissociation energies of the C-Br and C-I bonds (81 and 65 kcal mol<sup>-1</sup>, respectively)<sup>69</sup> (Table 3, compare entries 1-5 with 7-11). It is worth to note that, when 2-iodothiophene was used as coupling partner, 85% yield was obtained for (E)-methyl 3-(thiophen-2-yl)acrylate (5f), although longer reaction time (60 min) was required (Table 4, entry 6). This catalytic system was also applicable to the cross-coupling of n-butyl acrylate (Table 4, entries 12-20). Similarly, n-butyl acrylate was found to be extremely reactive substrate affording the relative product rapidly in the presence of ZrO<sub>2</sub>@ECP-Pd nanocatalyst (Table 4, entries 12-17). Meanwhile, with aryl bromides containing both electron withdrawing and electron donating groups, the reactions proceeded more slowly with lower yields of the desired products (Table 4, entries 18-20).

Under the same reaction conditions, we examined chlorobenzene for the Mizoroki-Heck reaction. It was observed that the poor yield of product was obtained in prolonged reaction time.

According to the results shown in Table 4, the generality of this protocol using the synthesized catalytic system is confirmed and good to excellent yields are obtained in the presence of ZrO<sub>2</sub>@ECP-Pd nanocatalyst.

 $R^2 = Me, Bu^n$ 

Table 3 The Mizoroki-Heck coupling reaction of iodobenzene with methyl acrylate in the presence of  $ZrO_2@ECP-Pd$  nanocatalyst under different reaction conditions.

Entry	Catalyst (mol %)	Solvent	Base	Temperature (°C)	Time (min)	Isolated Yield (%)
1	0.31	DMF	Et <sub>3</sub> N	90	30	90
2	0.31	CH <sub>3</sub> CN	Et <sub>3</sub> N	90	1(h)	60
3	0.31	$H_2O$	Et <sub>3</sub> N	90	3 (h)	50
4	0.31	EtOH	Et <sub>3</sub> N	90	1 (h)	75
5	0.31	[bmim]PF <sub>6</sub>	Et <sub>3</sub> N	90	1 (h)	90
6	0.31	[bmim]PF <sub>6</sub>	Et <sub>3</sub> N	100	30	95
7	0.31	[bmim]PF <sub>6</sub>	NaOAc	100	1 (h)	80
8	0.31	[bmim]PF <sub>6</sub>	$K_2CO_3$	100	1 (h)	50
9	0.40	[bmim]PF <sub>6</sub>	Et <sub>3</sub> N	100	30	95
10	0.15	[bmim]PF <sub>6</sub>	Et <sub>3</sub> N	100	30	80

Table 4 The Mizoroki-Heck cross-coupling reactions of olefins and aryl halides catalyzed by ZrO<sub>2</sub>@ECP-Pd nanocatalyst.

	1	$X = O = O R^2 - R^2$	ZrO <sub>2</sub> @ECP-Pd [bmim]PF <sub>6</sub> NEt <sub>3</sub> , 100 °C		DR <sup>2</sup>	
				5a-h		
Entry	$R^1$	$\mathbf{R}^2$	Х	Product	Time (min)	Isolated Yield (%)
1	Н	Me	Ι	5a	30	95
2	4-Cl	Me	Ι	5b	30	98
3	4-NO <sub>2</sub>	Me	Ι	5c	30	95
4	4-Me	Me	Ι	5d	30	95
5	4-OMe	Me	Ι	5e	30	92
6	2-Thiophene	Me	Ι	5f	60	85
7	Н	Me	Br	5a	180	80
8	4-NO <sub>2</sub>	Me	Br	5c	180	92
9	4-Cl	Me	Br	5b	180	94
10	4-CN	Me	Br	5g	180	85
11	4-OMe	Me	Br	5e	180	85
12	Н	$\operatorname{Bu}^n$	Ι	5h	30	95
13	4-NO <sub>2</sub>	$\operatorname{Bu}^n$	Ι	5i	30	96
14	4-Cl	$\operatorname{Bu}^n$	Ι	5j	30	94
15	4-OMe	$\operatorname{Bu}^n$	Ι	5k	45	90
16	4-Me	$\operatorname{Bu}^n$	Ι	51	40	95
17	2-Thiophene	$\operatorname{Bu}^n$	Ι	5m	120	80
18	Н	$\operatorname{Bu}^n$	Br	5h	180	75
19	4-NO <sub>2</sub>	$\operatorname{Bu}^n$	Br	5i	180	80
20	4-OMe	Bu <sup>n</sup>	Br	5k	180	70

#### **3.4 Heterogeneity Tests**

To determine whether the catalyst is actually functioning in a heterogeneous manner, a hot-filtration test was performed in the Suzuki-Miyaura coupling reaction of iodobenzene with phenylboronic acid. After 30 % conversion to product (5 min), the solid catalyst was separated from the reaction mixture by filtration. The reaction was carried out for a further 1h. No increase in the amount of product was observed, as determined by thin layer chromatography. In a separated test, a hot-filtration test was performed in the Mizoroki-Heck coupling reaction of iodobenzene with methyl acrylate. The same result was obtained from this reaction. So, it can be concluded that no leaching of palladium takes place during the reaction and that the catalyst is purely heterogeneous in nature.

In addition, one of the most common poisoning test to distinguish heterogeneous vs. homogeneous catalysts is the

use of Hg(0). The mercury poisoning test with Hg(0) is based on the deactivation of colloidal metal via amalgam formation, and, this test in general does not attack molecular metal species. In our study we also found that  $ZrO_2@ECP-Pd$ nanocatalyst (0.31 mol %) maintains its activity in the Suzuki coupling of iodobenzene with phenylboronic acid in the presence of a large excess of Hg(0) (Hg/Pd, 300:1) under the optimized reaction conditions, affording the corresponding biphenyl in excellent conversion.<sup>70</sup>

# 3.5 Recycling of the ZrO<sub>2</sub>@ECP-Pd nanocatalyst

As Pd salts are expensive and also some of them are toxic, their leaching into the reaction mixture could be a serious worry in viewpoint of green chemistry. In this regard, catalyst immobilization is a good opportunity to obtain materials that can be recovered and reused for several cycles with low leaching. We therefore turned attention to this feature of the present Pd nanocatalyst and examined the

possibility of recycling of nanocatalyst in the reaction of iodobenzene with phenylboronic acid under the optimized reaction conditions (Figure 5). In a typical experiment, after completion of the reaction, the coupled product was repeatedly extracted from the reaction mixture with ethyl acetate. The ZrO<sub>2</sub>@ECP-Pd nanocatalyst was recovered by centrifuge, washed with water (10 mL) and ethyl acetate (3×5 mL). The obtained catalyst was dried at 50 °C for overnight before being subjected to further coupling reaction. As shown in Figure 5, this catalyst can be reused six times without any significant loss in its activity in the Suzuki-Miyaura reaction. The good reusability may be attributed to the strong interaction of Pd nanoparticles with phosphine groups present on the surface of the ZrO<sub>2</sub> NPs, which could efficiently stabilize Pd particles and prevent the aggregation of Pd particles formed during the catalytic reaction.58, 71 The reusability was also confirmed by ICP analysis of reused ZrO<sub>2</sub>@ECP-Pd nanocatalyst, which proved the presence of  $0.55 \times 10^{-3}$  mol/g of palladium. Moreover, in order to investigate the structure of reused ZrO2@ECP-Pd nanocatalyst, the FT-IR analysis of the 6<sup>th</sup> reused nanocatalyst was recorded (Figure 1f). As can be seen, the shape, position and relative intensity of all characteristic peaks are well preserved. The results indicate no considerable changes were observed on the chemical structure of the reused nanocatalyst (Figure 1f).



**Figure 5.** The Suzuki-Miyaura reaction of iodobenzene with phenylboronic acid in the presence of reused ZrO<sub>2</sub>@ECP-Pd nanocatalyst.

#### 4. Conclusion

Suzuki-Miyaura and Mizoroki-Heck reactions using palladium immobilized on phosphine functionalized ZrO<sub>2</sub> NPs (ZrO<sub>2</sub>@ECP-Pd). As a novel heterogeneous catalyst, ZrO<sub>2</sub>@ECP-Pd was prepared and characterized by FT-IR, XRD, SEM, TEM, TGA and ICP techniques. It was found that ZrO<sub>2</sub>@ECP-Pd nanocatalyst with spherical shape and mean diameters of 10–40 nm was successfully synthesized. Then synthesized nanocatalyst has been used as an efficient catalyst for the Suzuki-Miyaura and Mizoroki-Heck reactions of various aryl halide derivatives (aryl iodides/bromides) under benign reaction conditions. Excellent yields of product, short reaction times, elimination of dangerous and harmful solvents, mild reaction conditions, simple workup procedures, and the potential reusability of the catalyst are the notable and valuable features of this methodology.

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# **Graphical Abstract**

# Green and efficient procedure for Suzuki-Miyaura and Mizoroki-Heck coupling reactions using palladium catalyst supported on phosphine functionalized ZrO<sub>2</sub> NPs (ZrO<sub>2</sub>@ECP-Pd) as a new reusable nanocatalyst

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New palladium catalyst supported on phosphine functionalized  $ZrO_2$  NPs ( $ZrO_2@ECP-Pd$ ) was synthesized and characterized.  $ZrO_2@ECP-Pd$  exhibited efficient catalytic activity in the Suzuki-Miyaura and Mizoroki-Heck coss-coupling reactions under benign reaction conditions. Additionally, the synthesized nanocatalyst can be recovered and reused for the subsequent reactions (at least six times) without any appreciable loss of efficiency.

