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## Mizoroki–Heck and Suzuki–Miyaura reactions mediated by poly(2-acrylamido-2-methyl-1-propanesulfonic acid)stabilized magnetically separable palladium catalyst

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**Funding information** Semnan University Research Council The purpose of this work was to synthesize and characterize a new magnetic polymer nanosphere-supported palladium(II) acetate catalyst for reactions requiring harsh conditions. In this regard, an air-stable, moisture-stable and highly efficient heterogenized palladium was synthesized by the coordination of palladium(II) acetate with poly(2-acrylamido-2-methyl-1-propanesulfonic acid)-grafted modified magnetic nanoparticles with a core-shell structure. The structure of the newly developed catalyst was characterized using various techniques. The catalytic activity of the resultant nano-organometallic catalyst was evaluated in Mizoroki–Heck and Suzuki–Miyaura reactions to afford the corresponding coupling products in good to excellent yields. High selectivity as well as outstanding turnover number (14 143, 4900) and turnover frequency (28 296, 7424) values were recorded for the catalyst in Suzuki–Miyaura and Mizoroki–Heck reactions, respectively. Magnetic separation and recycling of the catalyst for at least six runs became possible without any significant loss of efficiency or any detectable palladium leaching.

#### KEYWORDS

heterogeneous palladium catalyst, magnetic polymer-supported palladium, Mizoroki–Heck coupling reaction, Suzuki–Miyaura coupling reaction

## **1** | INTRODUCTION

One of the foundational reactions in organic synthesis is the formation of carbon–carbon bonds because of its many applications in the synthesis of numerous drugs, natural products and high-performance modern materials. The Mizoroki–Heck and Suzuki–Miyaura coupling reactions are particularly versatile methods for forming carbon–carbon bonds.<sup>[1]</sup> A significant number of reviews have focused on these reactions, due to their high impact and experimental importance in the generation of fine chemicals and pharmaceuticals.<sup>[2–4]</sup> In this regard, many effective catalytic systems have been designed and developed for this reaction. Palladium catalysis has emerged as one of the most powerful tools for carbon–carbon bond formation in organic synthesis.<sup>[5–8]</sup> Principally, the palladium-catalysed Mizoroki–Heck and Suzuki– Miyaura coupling reactions are carried out homogeneously in water,<sup>[9,10]</sup> organic media<sup>[11,12]</sup> or ionic liquids.<sup>[13,14]</sup> Although catalytic activities of homogeneous catalysts are higher than those of their heterogeneous counterparts, they suffer from important drawbacks such as laborious recovery and recycling of the catalyst, purification of final products and deactivation of the catalyst.<sup>[15]</sup> In addition, because of the high toxicity and cost of palladium, its removal from organic products at the end of a reaction is very important.<sup>[16]</sup> So, heterogeneous catalytic systems are drawing considerable attention due to the desirability of recovery and reuse of valuable palladium catalysts.

The immobilization of palladium on various solid supports has led to the development of several types of heterogeneous palladium catalysts.<sup>[17,18]</sup> The support is one of the most important and key factors in heterogeneous catalyst systems, because it plays a crucial role in longevity, conversion yield and thermal and mechanical stability of the catalyst.<sup>[19,20]</sup> These parameters principally determine whether a catalyst is practicable for industrial processes. Most supports are materials with properties like reusability, ready availability, eco-friendliness and low cost.<sup>[21,22]</sup> However, there are disadvantages from which these supported catalysts suffer, such as leaching of palladium from catalyst to reaction mixture and easy agglomeration. So, the development of new catalysts that are simultaneously active and stable, as well as easy to separate and reuse is of much importance as it will surely facilitate actual practical applications in carbon-carbon coupling reactions. The supported catalysts are based on inorganic,<sup>[23,24]</sup> (bio)organic<sup>[25,26]</sup> and hybrid structures.<sup>[27]</sup> The chemical and physical properties of hybrid organic-inorganic materials are not only the sum of the single contributions of both phases, but also the result of synergy of both parts, depending on the size distribution and spatial arrangement of their constituents, so hybrid materials play a vital role in the development of advanced functional materials.

In this regard, polymer grafting on inorganic, metal or carbon-based surfaces, known as polymer brushes, is of

particular importance in many fields of application.<sup>[28,29]</sup> Polymers tethered to inorganic surfaces like SiO<sub>2</sub>,<sup>[30]</sup> Fe<sub>3</sub>O<sub>4</sub>,<sup>[31,32]</sup> ZnO,<sup>[33]</sup> Au<sup>[34]</sup> or alumina<sup>[35]</sup> have attracted extensive research interest due to the ability to modify the surface characteristics and have applications in basic and applied interfacial studies. One of the most promising support matrices, for incorporation of polymer species, is superparamagnetic iron oxide nanoparticles with high surface area, which are easily obtained from commercially available materials such as FeCl<sub>3</sub>·6H<sub>2</sub>O and FeCl<sub>2</sub>·4H<sub>2</sub>O in water.<sup>[36]</sup> The facile recovery of a catalyst that can be manipulated using magnetic fields is the prime advantage of using magnetic nanoparticles (MNPs) as supports, for which the catalyst loss problem during the filtration at the end of the reaction is solved. The convenient functionality of MNPs with various coupling agents is another advantage, because they prevent the catalyst from leaching during the reaction due to the strong chemical interaction between the organocatalyst and the metallic support. So, polymer-MNP composites have emerged as promising and robust materials because they combine the advantages of MNPs (e.g. thermal stability, large surface area and magnetic properties) and organic polymers (e.g. pH stability and chemical functionality). There are three methods of synthesis, 'grafting to',<sup>[37]</sup> 'grafting from'<sup>[38]</sup> and 'grafting through',<sup>[39]</sup> that are used to construct a graft polymer. Figure 1 illustrates various strategies for surface grafting with a polymer.

Considerable effort has been made over time to develop more palladium–polymer hybrid catalysts.<sup>[40–42]</sup>



**FIGURE 1** The most common techniques of polymer grafting

Despite the considerable success achieved in the field of polymeric stabilizers, it is a challenging task to develop hydrophilic functional groups attached to a polymeric backbone, such as -COOH, -SO<sub>3</sub>H, -CONH<sub>2</sub>, -NH<sub>2</sub> and -OH, for the incorporation of metals, especially in the case of Mizoroki-Heck and Suzuki-Miyaura coupling reactions. In this paper, we introduce the design of a highly dispersed catalytic system in green environment which can be separated from a reaction mixture and recycled easily several times without considerable loss of its catalytic activity. In this line, we report a novel catalytic system, denoted as MNP@PAMPS-Pd(II), involving Pd(II) supported on poly(2-acrylamido-2-methyl-1propanesulfonic acid) (PAMPS)-grafted modified MNPs with a core-shell structure. To the best of our knowledge, there are no literature reports on the synthesis of PAMPSgrafted modified MNPs with a core-shell structure through a 'grafting from' approach. Finally, we report a study of the efficiency of our new and reusable catalyst in the Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions. High turnover number (TON) and turnover frequency (TOF) values were exciting results for the catalyst in both reactions. Catalysts with  $TON > 10^3$ are deemed as HTC supports.<sup>[43]</sup>

#### 2 | EXPERIMENTAL

#### 2.1 | General Remarks

The chemicals, reagents and solvents were employed without further purification and purchased from Merck and Sigma-Aldrich. Fourier transform infrared (FT-IR) spectra were recorded with a Shimadzu 8400 s spectrometer using KBr pressed powder discs. Magnetic measurements were carried out using vibrating sample magnetometry (VSM; Lakeshore 7407) at room temperature. The crystalline structures of the samples were evaluated by X-ray diffraction (XRD) analysis at room temperature on with a Siemens D5000 (Siemens AG, Munich, Germany) using Cu Ka radiation of wavelength of 1.54 Å. Field-emission scanning electron microscopy (Fe-SEM) and energy-dispersive X-ray (EDX) analysis were done to obtain information about the particle size, morphology and elemental mapping of the catalyst using a TESCAN MIRA II digital scanning microscope. Transmission electron microscopy (TEM) images were obtained with a CM120 microscope (Philips). The purity of products was determined using TLC on commercial plates coated with silica gel 60 F254 using n-hexane-ethyl acetate mixture as the mobile phase. Thermogravimetric analysis (TGA) was done using a DuPont 2000 thermal analysis apparatus heated from 25 to 1000 °C at a ramp of 5 °C min<sup>-1</sup> under air atmosphere. The amount of WILEY Organometallic 3 of 16

palladium in the catalyst was measured using inductively coupled plasma optical emission spectrometry (ICP-OES) with a Varian VISTA-PRO. NMR spectra were measured in pure dimethylsulfoxide (DMSO) with a Bruker Advance 400 MHz instrument (<sup>1</sup>H NMR: 400 MHz; <sup>13</sup>C NMR: 125 MHz) with tetramethylsilane as the internal reference. Detection of products was performed with a gas chromatograph (GC-17A, Shimadzu, Japan) equipped with a splitless/split injector and a flame ionization detector. Helium (purity 99.999%) was used as the carrier gas at a constant flow rate of 4 ml min $^{-1}$ . The temperatures of injector and detector were set at 275 and 320 °C, respectively. The injection port was operated in splitless mode and with sampling time of 1 min. For flame ionization detection, hydrogen gas was generated with a hydrogen generator (OPGU-2200S, Shimadzu, Japan). A 30 m BP-10 SGE fused-silica capillary column (0.32 mm i.d. and 0.25 µm film thickness) was applied for separation of products. Oven temperature programme was: started from 60 °C, held for 3 min, increased to 190 °C at 20 °C min<sup>-1</sup>, held for 0 min, increased to 240 °C at 10 °C min<sup>-1</sup> and then held for 3 min. A 10.0  $\mu$ l ITO (Fuji, Japan) micro-syringe was applied for the collection of sedimented organic solvent and injection into the chromatograph.

## 2.2 | Catalyst Preparation

## 2.2.1 | Synthesis of modified magnetic nanoparticles (MNP@IA)

In order to increase the stability, impede the agglomeration of MNPs and provide reactive C=C bonds, the surface of Fe<sub>3</sub>O<sub>4</sub> nanoparticles was modified with itaconic acid (IA). For this purpose, magnetite nanoparticles were prepared using a modified procedure based on a previously reported method.<sup>[44]</sup> In a typical synthesis, 2.5 mmol of FeCl<sub>2</sub>·4H<sub>2</sub>O and 5.0 mmol of FeCl<sub>3</sub>·6H<sub>2</sub>O were dissolved in 10 ml of ultrapure water. This solution was added dropwise into an aqueous solution of ammonium hydroxide (2 wt%) at 90 °C under vigorous magnetic stirring. After 30 min, the black material formed was collected with a magnet to remove the supernatant. All steps were performed under nitrogen atmosphere. The modification of the iron oxide particles was then achieved by adding a mixture of 0.7 mmol of IA dissolved in 5.0 ml of an aqueous solution of ammonia (2 wt%). After 1 h of stirring at 50 °C, the modified MNP@IA was obtained, which was magnetically separated, washed three times with ethanol and deionized water to remove any excess reagent and salts, and then dried in a vacuum oven overnight.

# 2.2.2 | Polymerization and synthesis of MNP@PAMPS nanocomposite

For the polymerization of the desired monomers on the surface of the modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles, in a typical 2-acrylamido-2-methyl-1-propanesulfonic experiment, acid (AMPS; 1.0 g) was added to a flask containing 1 g of modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles suspended in 12 ml of deionized water. Then, the mixture was purged under nitrogen gas for 15 min to remove dissolved oxygen. Subsequently, 0.053 g of ammonium persulfate as an initiator was added to the reaction mixture, and kept at 60 °C for 24 h to complete the polymerization. Finally, the obtained PAMPS-coated MNPs were separated from the suspension using an external magnet and washed with ethanol and water (three times) to eliminate excess reactants and then dried in a vacuum oven for 24 h at 50 °C to afford the MNP@PAMPS nanocomposite.

## 2.2.3 | Synthesis of Pd(II) supported on PAMPS-grafted modified MNPs (MNP@PAMPS-Pd(II))

MNP@PAMPS (0.5 g),  $Pd(OAc)_2$  (0.1 g) and deionized water (50 ml) were placed into a round-bottom flask and sonicated for 45 min. Then, the reaction was left to stir for 12 h at room temperature. The final palladium complex (MNP@PAMPS-Pd(II)) was magnetically separated and washed several times with distilled water, ethanol and acetonitrile for any excess reagent to be removed and finally dried in a vacuum oven at 60 °C for 24 h.

## 2.3 | Investigations of Catalytic Activity

## 2.3.1 | MNP@PAMPS-Pd(II)-catalysed Suzuki–Miyaura reaction: general procedure

A mixture of phenylboronic acid (1.2 mmol), aryl halide (1.0 mmol),  $K_2CO_3$  (3.0 mmol) and MNP@PAMPS-Pd(II) (0.007 mol%) as catalyst in 5 ml of ethanol-water (1: 1) was added to a round-bottom flask with a magnetic stirrer and placed in an oil bath to keep the temperature at reflux temperature (80 °C) for the required period of time (reaction was monitored by TLC). After the completion of the reaction, the catalyst was separated using an external magnet. Then, after the reaction mixture was cooled to room temperature, it was extracted with ethyl acetate. After the extraction of the aqueous layer, the organic layer was washed with water and dried over anhydrous MgSO<sub>4</sub>. Some products were characterized using GC-FID and <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopic techniques and the results are presented in the supporting information.

## 2.3.2 | MNP@PAMPS-Pd(II)-catalysed Mizoroki-Heck reaction: general procedure

A mixture of aryl halide (1.0 mmol), olefin (1.5 mmol),  $K_2CO_3$ (2.0)mmol) and MNP@PAMPS-Pd(II) (0.02 mol%) as catalyst in 3 ml of dimethylformamide (DMF) was added to a round-bottom flask with a magnetic stirrer. The mixture was stirred at 100 °C for an appropriate time. After the completion of the reaction as monitored by TLC, the magnetic catalyst was separated using an external magnet and the reaction mixture was cooled to room temperature. The reaction mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous MgSO<sub>4</sub>. Some products were characterized using <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectroscopic techniques and the results are presented in the supporting information.

## 2.3.3 | Reusability of catalyst

Reusability of the nanocatalyst was investigated using the reaction of iodobenzene with phenylboronic acid under already determined optimized conditions. At the end of the reaction, the separated catalyst was washed with water and ethanol to remove salt and adsorbed organic substrates, respectively, and reused in subsequent runs with new portions of reagents without any pre-treatment.

## 3 | RESULTS AND DISCUSSION

# 3.1 | Synthesis and Characterization of MNP@PAMPS-Pd(II)

As already mentioned, several types of heterogeneous palladium catalysts have been developed by immobilizing palladium on various solid supports. So, the aim of the study reported here was to develop a new system of palladium immobilized onto a suitable support to overcome most of the problems associated with the use of homogeneous palladium catalysts. In this line, we decided to synthesize a novel polymer-stabilized magnetically separable palladium catalyst. Design of the heterogeneous Pd(II) catalyst was carried out according to a concise route, as outlined in Scheme 1. Initially, before coating of the polymer onto the Fe<sub>3</sub>O<sub>4</sub> surface, the surface of the MNPs was modified with IA to give reactive C=C bonds on the surface of Fe<sub>3</sub>O<sub>4</sub>. The presence of vinyl groups on the surface of Fe<sub>3</sub>O<sub>4</sub> gives two important results. First, it makes polymerization easier on the surface of MNPs. The copolymer is grafted onto the surface of MNP through covalent bonds.<sup>[45]</sup> Second, without IA modification, only a minor part of the MNPs can be coated with a complete layer of polymer chains.<sup>[45]</sup> Subsequently, the MNP@PAMPS



**SCHEME 1** Procedure for preparation of MNP@PAMPS-Pd(II)

nanocomposite was obtained by the polymerization of AMPS as a monomer in the presence of modified Fe<sub>3</sub>O<sub>4</sub> using ammonium persulfate as an initiator for radical polymerization to produce the desired polymer. Finally, the resulting MNP@PAMPS was reacted with palladium acetate in water to form the MNP@PAMPS-Pd(II) catalyst. As one can see, PAMPS as a ligand carrying SO<sub>3</sub>H and CONH<sub>2</sub> functional groups could immobilize palladium, through oxygen and nitrogen atoms.<sup>[46]</sup> Therefore, there is no need for an additional ligand. Furthermore, PAMPS has hydrophilic character which can be considered as another important reason for choosing this polymer as polymeric segment. The amount of palladium loaded was found to be 0.73 mmol  $g^{-1}$  (determined by ICP-OES analysis). As can be seen, the palladium content of the catalyst is very significant compared to that of some other solid-supported palladium complexes, which can be due to multilayer and polymeric nature of the coated material on the surface of the MNPs that allows many functional groups to immobilize palladium. To prove the structure of catalyst, elucidate any errors during the preparation procedure and investigate the stability of the catalyst before and after the catalytic reaction, a comprehensive characterization was achieved using FT-IR spectroscopy, XRD, TGA, TEM, VSM, FE-SEM, ICP-OES and EDX analysis.

#### 3.1.1 | FT-IR spectra

The FT-IR spectra of  $Fe_3O_4$ , AMPS, MNP@PAMPS and MNP@PAMPS-Pd(II) are depicted in Figure 2 to confirm the modification of the magnetite surface with the organic polymer shell. All magnetic samples show two bands at around 557 and 570 cm<sup>-1</sup>, corresponding to Fe—O stretching vibration (Figure 2a,c,d). After the



**FIGURE 2** FT-IR spectra of (a) Fe<sub>3</sub>O<sub>4</sub> nanoparticles, (b) AMPS, (c) MNP@PAMPS and (d) MNP@PAMPS-Pd(II)

polymerization process, characteristic absorption peaks at 1041 and 1120 cm<sup>-1</sup> are attributed to the stretching vibrations of S=O of sulfonic acid, associated with PAMPS (Figure 2b,c). The bands at 1400 and 1635  $\text{cm}^{-1}$  result from the stretching of C-N and stretching of amidic C=O bonds, respectively (Figure 2b,c). In addition, the broad band between 3600 and 3000  $\text{cm}^{-1}$  is attributed to the stretching of O-H and N-H bonds. These results show the MNPs were successfully coated with the polymer. Following metal complexation, the intensities and locations of the bands at 1400 and 1120 cm<sup>-1</sup> were changed. The intensity of the peak at approximately 1400 cm<sup>-1</sup> assigned to the stretching of C-N band became weaker than that for MNP@PAMPS, and the band was shifted to lower wavenumber, 1398  $\text{cm}^{-1}$ , due to the coordination of palladium ions to the ligand via donor nitrogen atoms. An apparent intensity decrease was recorded for the band at  $1120 \text{ cm}^{-1}$  due to asymmetric  $-SO_2$  stretching and a shift to 1116 cm<sup>-1</sup>, indicating the occurrence of the palladium complex (Figure 2d).

## 3.1.2 | XRD analysis

The XRD pattern of the supported palladium catalyst exhibits diffraction peaks at around  $30.5^{\circ}$ ,  $35.9^{\circ}$ ,  $43.5^{\circ}$ ,  $53.9^{\circ}$ ,  $57.2^{\circ}$  and  $63^{\circ}$  ( $2\theta$ ) ascribed to the inverse cubic spinel structure of Fe<sub>3</sub>O<sub>4</sub>, which is consistent with the standard Fe<sub>3</sub>O<sub>4</sub> XRD pattern (Figure 3).<sup>[47]</sup> As illustrated in Figure 3, the surface modification of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles did not lead to a phase change. Furthermore, no peak characteristic for Pd<sup>0</sup> nanoparticles was observed. So, the XRD pattern confirms that the loading of Pd(II) on the catalyst was successful.

## 3.1.3 | Thermal analysis

The thermal degradation of MNP@PAMPS and MNP@PAMPS-Pd(II) was investigated using TGA to study the composition and weight loss at different decomposition temperatures of the desired nanocatalyst (Figure 4). Both materials show three main decomposition stages. The first



FIGURE 3 XRD pattern of (a)  $Fe_3O_4$  nanoparticles and (b) MNP@PAMPS-Pd(II)



**FIGURE 4** TGA curves of (a) MNP@PAMPS and (b) MNP@PAMPS-Pd(II)

decomposition step (under 200 °C) corresponds to the removal of physically adsorbed water. The second step of weight loss (about 220-295 °C) is related to the decomposition of sulfonate groups, associated with PAMPS.<sup>[48]</sup> The third thermal degradation at about 400 °C is ascribed to main-chain degradation of immobilized polymer on the surface of MNPs.<sup>[48]</sup> According to Figure 4(a), the amount of organic components loaded on the surface of MNPs can be calculated approximately. The observed total weight loss between 200 and 800 °C for MNP@PAMPS is 26%, which is attributed to the polymeric moieties. Comparing with the TGA curve of AMPS,<sup>[49]</sup> the thermal stability of the magnetic polymer is intensified markedly, which is possibly due to PAMPS chemically bonded to the surface of the modified Fe<sub>3</sub>O<sub>4</sub> nanoparticles. A closer inspection of the TGA curve of MNP@PAMPS-Pd(II) shows slightly lower thermal stability after the immobilization of palladium ions, which can be due to the coordination of the metal ions with the ligands<sup>[50]</sup> and the catalytic effect of palladium ions in the decomposition of the polymeric structure.<sup>[51]</sup> Still, this thermal stability is very acceptable for the catalyst application, such as C-C coupling reactions, which are carried out at high temperatures. Also, when compared to the percentage of the remaining mass of MNP@PAMPS (ca 62%) (Figure 4a), MNP@PAMPS-Pd(II) has higher undecomposed content (ca 80%). This difference can be attributed to the amount of loaded palladium and polymeric moieties in the structure of the catalyst.

#### 3.1.4 | Vibrating sample magnetometry

In order to assay the effect of the polymeric moieties and immobilization of palladium ions on the magnetic properties of the  $Fe_3O_4$  nanoparticles, the magnetic properties of bare  $Fe_3O_4$  nanoparticles and MNP@PAMPS-Pd(II) were measured via VSM at room temperature (Figure 5). As shown in Figure 5, the magnetic saturation value markedly decreased to 30 emu g<sup>-1</sup> for MNP@PAMPS-



**FIGURE 5** Room temperature magnetization curves of (a) Fe<sub>3</sub>O<sub>4</sub> nanoparticles and (b) MNP@PAMPS-Pd(II)

Pd(II). This significant decrease may be assigned to the fact that the  $Fe_3O_4$  nanoparticles were coated entirely by an inert organic shell. However, the level of catalyst magnetization is still adequate, so that when a magnet is

WILEY Organometallic 7 of 16 Chemistry

placed beside a vial containing a suspension of MNP@PAMPS-Pd(II) nanocomposite spheres, the nanocomposites are quickly attracted to the side of the vial within a few seconds (Figure 5, inset).

## 3.1.5 | Field-emission scanning electron microscopy

The morphology and particle shape of MNP@PAMPS-Pd(II) were studied using FE-SEM (Figure 6d). As can be seen, the morphology of MNP@PAMPS-Pd(II) is completely different from those of the ligands<sup>[52]</sup> (Figure 6 a,b) and Fe<sub>3</sub>O<sub>4</sub> nanoparticles (Figure 6c). These observations demonstrate that PAMPS was successfully linked to Fe<sub>3</sub>O<sub>4</sub> nanoparticles and palladium ions were coordinated with the ligands. The FE-SEM image of MNP@PAMPS-Pd(II) (Figure 6d) illustrates that the catalyst particles are quasi-spherical. The image shows the presence of the composite on the nanometre-sized particles.



FIGURE 6 FE-SEM images of (a) PAMPS, (b) P(AMPS-co-IA), (c) Fe<sub>3</sub>O<sub>4</sub> nanoparticles and (d) MNP@PAMPS-Pd(II)



FIGURE 7 EDX spectrum of MNP@PAMPS-Pd(II)

#### 3.1.6 | EDX analysis

MNP@PAMPS-Pd(II) was analysed for its chemical composition through EDX analysis to verify the successful incorporation of polymeric segments on  $Fe_3O_4$  surface and palladium attachment to them. The EDX spectrum (Figure 7) indicated the presence of the Pd as well as C, N, O, S and Fe in the body of the catalyst. The amount of Pd(II) supported onto the PAMPS-grafted modified MNPs was determined as 7.7% (based on EDX results).

#### 3.1.7 | Transmission electron microscopy

Further characterization of MNP@PAMPS-Pd(II) was performed using TEM. From the TEM images of MNP@PAMPS-Pd(II) (Figure 8), it could be seen that the morphology of MNP@PAMPS-Pd(II) remained almost the same after loading Pd(OAc)<sub>2</sub> on MNP@PAMPS.

## 3.1.8 | ICP-OES analysis

ICP-OES analysis was used to explore the palladium content of the supported catalyst. The amount of palladium in the catalyst was determined to be 0.73 mmol  $g^{-1}$  which is in good agreement with the result of EDX analysis.

## 3.2 | Effectiveness of MNP@PAMPS-Pd(II) in C-C Coupling Reactions

After the novel nanocomposite was fully characterized with various techniques, its catalytic activity was studied in C—C coupling reactions. A versatile polymer-supported heterogeneous palladium catalyst for Mizoroki–Heck and Suzuki–Miyaura reactions has been introduced.<sup>[53,54]</sup> But, to the best of our knowledge, few successful examples of hydrophilic polymer-stabilized magnetically separable palladium materials to catalyse Suzuki–Miyaura and Mizoroki–Heck



FIGURE 8 (a, b) TEM images of MNP@PAMPS-Pd(II)

reactions under green conditions have been reported.<sup>[55–57]</sup> So, to investigate the performance of the catalyst, we evaluated its catalytic activity in C—C coupling reactions, not only for Suzuki–Miyaura cross-coupling of aryl halides and phenylboronic acid (Scheme 2), but also for Mizoroki–Heck reactions of aryl halides and activated alkenes (Scheme 3).

## 3.2.1 | Optimization of reaction parameters for Suzuki-Miyaura coupling reaction

In the palladium-catalysed Suzuki C—C coupling reactions, parameters like the amount of the catalyst, solvent, reaction time, temperature and base system are important. So, these parameters should be optimized before the catalytic activity determination is performed. The effect of various parameters on Suzuki–Miyaura crosscoupling of iodobenzene with phenylboronic acid in the presence our new catalytic system as a model reaction was investigated and the results are as follows.



SCHEME 3 MNP@PAMPS-Pd(II)catalysed Mizoroki–Heck reaction

SCHEME 2 MNP@PAMPS-Pd(II)-

catalysed Suzuki-Miyaura reaction

#### Effect of amount of MNP@PAMPS-Pd(II) catalyst

To determine the suitable catalyst loading, the model reaction was carried out with different amounts of the catalyst added. The results are summarized in Table 1. Initially, the model reaction was carried out in the absence of the catalyst. As expected, no product was observed in the absence of the catalyst. As can be seen, as the amount of catalyst increased from 0.005 to 0.01 mol%, the product yield increased, which is probably due to the availability of more catalytic sites. According to the results, 0.007 mol% was chosen as the optimum amount of catalyst, affording the best product yield.

#### Effect of solvent

Solvents can allow thermodynamic and kinetic control over a chemical reaction, so the choice of an appropriate solvent is very important. Thus, the model reaction was carried out in conventional solvents to obtain the best catalytic conversion. As can be seen from Table 1, this reaction proceeded faster, more cleanly and in higher yields when the reaction was conducted in a mixture of  $H_2O$ and EtOH in 1:1 ratio as solvent. Because of the hydrophilic character of polymer-stabilized palladium, water solubility of boronic acid and hydrophobic character of aryl halides, the choice of this solvent mixture provides a good interaction between them, which leads to an improvement in the Suzuki–Miyaura reaction.

#### Effect of base

Base is one part of the catalytic mechanism and it should exhibit high efficiency and be of low cost. So, the reaction is significantly affected by the nature of the base and the additive used. Therefore, a variety of bases were evaluated. As can be seen from Table 1, the best performance occurred with  $K_2CO_3$ .

#### Effect of time and temperature

Temperature affects the kinetics of a reaction crucially. Also, shorter reaction times are desired for catalysis systems to decrease labour and operational cost. Hence, in order to investigate the effect of these two parameters, the model reaction was carried out at different temperatures for different times. According to Table 1, the best choice was 80 °C as the optimal temperature when the reaction continued for 30 min.

Consequently, the optimum reaction conditions were determined as: 0.007 mol% of the catalyst (MNP@PAMPS-Pd(II)) in 5 ml of EtOH-H<sub>2</sub>O (1:1) at

**TABLE 1** Optimization of reaction conditions for Suzuki-Miyaura reaction of iodobenzene with phenylboronic acid catalysed byMNP@PAMPS-Pd(II)

Entry	Amount of catalyst (mol%)	Solvent	Temperature (°C)	Base	Time (min)	Yield (%)
1	0	H <sub>2</sub> O	25	K <sub>2</sub> CO <sub>3</sub>	120	0
2	0.005	H <sub>2</sub> O	25	K <sub>2</sub> CO <sub>3</sub>	40	65
3	0.007	$H_2O$	25	K <sub>2</sub> CO <sub>3</sub>	30	75
4	0.01	H <sub>2</sub> O	25	K <sub>2</sub> CO <sub>3</sub>	30	75
5	0.007	EtOH	25	K <sub>2</sub> CO <sub>3</sub>	30	52
6	0.007	H <sub>2</sub> O-EtOH (1/1)	25	K <sub>2</sub> CO <sub>3</sub>	30	90
7	0.007	CH <sub>3</sub> COOEt	25	K <sub>2</sub> CO <sub>3</sub>	30	70
8	0.007	H <sub>2</sub> O-EtOH (1/1)	25	Na <sub>2</sub> CO <sub>3</sub>	30	40
9	0.007	H <sub>2</sub> O-EtOH (1/1)	25	КОН	30	57
10	0.007	H <sub>2</sub> O-EtOH (1/1)	25	NaOH	30	45
11	0.007	H <sub>2</sub> O-EtOH (1/1)	60	K <sub>2</sub> CO <sub>3</sub>	30	95
12	0.007	H <sub>2</sub> O-EtOH (1/1)	80	K <sub>2</sub> CO <sub>3</sub>	30	98
13	0.007	H <sub>2</sub> O-EtOH (1/1)	100	K <sub>2</sub> CO <sub>3</sub>	30	99

10 of 16 WILEY

reflux temperature (80 °C) and 3.0 mmol of K<sub>2</sub>CO<sub>3</sub> as a base in the reaction of iodobenzene (1.0 mmol) and phenyl boronic acid (1.2 mmol).

## 3.2.2 | Performance of catalyst with several substrates for Suzuki-Miyaura reaction

After the optimization of the reaction conditions, to explore the scope of this reaction and screen the efficiency of our novel nanocatalyst, we extended the substrate scope to various aryl halides (aryl bromides, aryl chlorides and aryl iodides) with phenylboronic acid for the Suzuki-Miyaura reaction (Scheme 2). These findings are summarized in Table 2. In most cases, good to excellent yields were obtained. It is noteworthy that aryl chloride reacts with more difficult and in longer reaction times compared to aryl bromide and aryl iodide. This difference is due to stronger C-Cl bond than C-Br and C-I, or, in other words, chlorides have high bond dissociation energy. Turnover number (TON) and turnover frequency (TOF) were calculated for all products as listed in Table 2. As can be seen, the catalyst yielded remarkable TONs and TOFs.

## 3.2.3 | Optimization of reaction parameters for Mizoroki-Heck reaction

Following the excellent results obtained for the Suzuki-Miyaura reaction, we were encouraged to examine the

#### Effect of amount of MNP@PAMPS-Pd(II) catalyst

Our efforts were focused on optimizing conditions for C-C coupling reaction of iodobenzene with methyl acrylate by using different amounts of MNP@PAMPS-Pd(II) to determine their effects on the reaction (Table 3). As can be seen, as the amount of catalyst increased from 0.005 to 0.03 mol%, the product yield increased from 55 to 95%, which is probably due to the availability of more catalytic sites. According to the results, 0.02 mol% was chosen as the optimum amount of catalyst, affording the best vield.

#### Effect of solvent

In order to investigate the effect of solvents, the model reaction was carried out in conventional organic solvents such as DMF, EtOH, H<sub>2</sub>O, MeOH and DMSO at 85 °C. According to the results in Table 3, DMF is the best solvent for the reaction.

#### Effect of base

The utilization of a base in the Mizoroki-Heck reaction is essential to neutralize hydrogen halides and prevent homo-coupling product formation.<sup>[42]</sup> So, the effect of different bases for the model reaction was further

**TABLE 2** Effect of MNP@PAMPS-Pd(II) on coupling of aryl halides with  $PhB(OH)_2^a$ 

Entry	Aryl halide	Product	Time (min) <sup>b</sup>	Yield (%) <sup>c</sup>	M.p. (°C)	TON <sup>d</sup>	TOF <sup>d</sup>
1			30	99	69	14 143	28 286
2	H <sub>3</sub> CO-	H <sub>3</sub> CO	30	92	87–90	13 143	26 286
3	Br Br		40	95	70	13 571	20 255
4	H <sub>3</sub> CBr	H <sub>3</sub> C	45	90	45-47	12 857	17 143
5	O <sub>2</sub> N-Br	0 <sub>2</sub> N-	30	98	111–113	14 000	28 000
6	IBr	Br	35	96	82-85	13 714	23 645
7	CI CI	$\overline{}$	120	60	69	8 571	4 286
8 <sup>e</sup>			60	50	69	7 143	7 143

<sup>a</sup>Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (3 mmol), catalyst (0.007 mol%) and EtOH-H<sub>2</sub>O (1:1) (5 ml), at 80 °C. <sup>b</sup>Detected by TLC.

<sup>c</sup>Isolated yield.

<sup>d</sup>TON, turnover number: yield of product per mole of Pd. TOF, turnover frequency: TON/time of reaction (h).

eIn the presence of excess mercury.

**TABLE 3** Optimization of reaction conditions for Mizoroki-Heck reaction of iodobenzene with methyl acrylate catalysed by

 MNP@PAMPS-Pd(II)

Entry	Amount of catalyst (mol%)	Solvent	Temperature (°C)	Base	Time (min)	Yield (%)
1	0.005	DMF	85	K <sub>2</sub> CO <sub>3</sub>	70	55
2	0.01	DMF	85	K <sub>2</sub> CO <sub>3</sub>	70	60
3	0.02	DMF	85	K <sub>2</sub> CO <sub>3</sub>	40	95
4	0.03	DMF	85	K <sub>2</sub> CO <sub>3</sub>	35	95
5	0.02	DMSO	85	K <sub>2</sub> CO <sub>3</sub>	50	87
6	0.02	МеОН	85	K <sub>2</sub> CO <sub>3</sub>	60	80
7	0.02	$H_2O$	85	K <sub>2</sub> CO <sub>3</sub>	60	50
8	0.02	EtOH	85	Na <sub>2</sub> CO <sub>3</sub>	60	58
9	0.02	DMF	85	КОН	60	90
10	0.02	DMF	85	NaOH	60	75
11	0.02	DMF	85	K <sub>2</sub> CO <sub>3</sub>	60	40
12	0.02	DMF	70	K <sub>2</sub> CO <sub>3</sub>	60	90
13	0.02	DMF	100	K <sub>2</sub> CO <sub>3</sub>	40	98
14	0.02	DMF	110	K <sub>2</sub> CO <sub>3</sub>	35	98

investigated. As can be seen from Table 3, the best performance occurred with  $K_2CO_3$ .

#### **Effect of temperature**

Because of the importance of temperature for the Mizoroki–Heck reaction, after the optimization of other parameters, the model reaction was investigated at various temperatures. According to Table 3, the best performance in terms of high yield occurred at 100 °C. Thus, 100 °C was considered as an optimum reaction temperature.

Consequently, the optimum reaction conditions for the Mizoroki–Heck reaction were determined as: 0.02 mol% of the catalyst (MNP@PAMPS-Pd(II)) in 3 ml of DMF at 100 °C and 2.0 mmol of K<sub>2</sub>CO<sub>3</sub> as a base in the reaction of iodobenzene (1.0 mmol) and methyl acrylate (1.5 mmol).

## 3.2.4 | Performance of catalyst with several substrates for Mizoroki–Heck reaction

In the final step, to broaden the scope of this new protocol, the Mizoroki–Heck reaction was carried out by employing various aryl halides with a variety of olefins (Scheme 3). As is evident from Table 4, almost all reactions gave good to excellent yields. The results show that aryl chloride reacts more slowly than aryl bromide and aryl iodide. Since oxidative addition is the first step in catalytic coupling reactions, it is not favoured with aryl chloride substrates because of the high strength of the C—Cl bond. Aryl chlorides are an ideal substrate for coupling reactions in comparison with other aryl halides (aryl bromide and aryl iodide) because they are inexpensive and widely available. Therefore, their use in coupling reactions is significant. Most reported methods require harsh conditions and high loadings of palladium catalyst. Nevertheless, those catalysts show little or no activity with aryl chloride substrates. In contrast, in the present method, Mizoroki–Heck coupling of even less reactive aryl chloride with olefin gives good yield as evident from Table 4. As is clear from Table 4, the achieved TONs and TOFs are very favourable.

## 3.3 | Comparison of Results Using MNP@PAMPS-Pd(II) With Results Obtained by Other Workers for the Mizoroki-Heck and Suzuki-Miyaura Reactions

The efficiency of the MNP@PAMPS-Pd(II) catalyst in the Suzuki–Miyaura reaction (Table 5) and the Mizoroki–Heck reaction (Table 6) was compared with that of some previously reported palladium-supported catalysts. Present protocol and catalyst have the advantages of magnetic recyclability, using a small amount of the catalyst, shorter reaction time, using a green solvent without any additional instrumentation such as a microwave oven, and high product yield. Therefore, it can be seen that MNP@PAMPS-Pd(II) is a very beneficial and advantageous catalyst in the Mizoroki–Heck and Suzuki–Miyaura reactions.

### **TABLE 4** Mizoroki–Heck coupling reactions of aryl halides with olefins<sup>a</sup>

Entry	Aryl halide	Olefin	Product	Time (min) <sup>b</sup>	Yield (%) <sup>c</sup>	M.p. (°C)	TON <sup>d</sup>	TOF <sup>d</sup>
1		COOMe	COOMe	40	98	35–39	4 900	7 424
2	Br	COOMe	COOMe	50	95	34–38	4 750	5 722
3	I-Br	COOMe	Br	40	95	83-86	4 750	7 196
4	H <sub>3</sub> CBr	COOMe	H <sub>3</sub> C COOMe	45	96	60–63	4 800	6 400
5	CI	COOMe	COOMe	120	73	35–39	3 650	1 825
6		СООВи	СООВи	40	97	140–142	4 850	7 348
7	Br Br	СООВи	СООВи	45	94	140–142	4 700	6 266

<sup>a</sup>Reaction conditions: aryl halide (1.0 mmol), olefin (1.5 mmol),  $K_2CO_3$  (2.0 mmol), catalyst (0.02 mol%) and DMF (3 ml), at 100 °C.

<sup>b</sup>Detected by TLC.

<sup>c</sup>Isolated yield.

<sup>d</sup>TON, turnover number: yield of product per mole of Pd. TOF, turnover frequency: TON/time of reaction (h).

Entry	Catalyst	Conditions	Time (h (min))	Yield (%)	Ref.
	+	B(OH) <sub>2</sub> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub> <u>B(OH)<sub>2</sub></u> <u>B(OH)<sub>2</sub> </u> <u>B(OH)<sub>2</sub> <u>B(OH)<sub>2</sub> </u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> <u>B(OH)2</u> </u></u></u></u></u>			
1	Pd-imino-Py- $\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	100 °C/DMF	(30)	95	[58]
2	Pd-ATBA-MNPs	100 °C/PEG	(40)	97	[59]
3	GO/Fe <sub>3</sub> O <sub>4</sub> /PAMPS/Pd	80 °C/EtOH-H <sub>2</sub> O	2	100	[46]
4	Pd/CNFs	80 °C/EtOH–H <sub>2</sub> O	4	99	[60]
5	Pd@CC-SO <sub>3</sub> H-NH	100 °C/H <sub>2</sub> O	2	96	[61]
6	$[\kappa^3$ - <i>N</i> , <i>N'</i> , <i>O</i> -Pd(1 $\subset$ 2)H <sub>2</sub> O]OAc	25 °C/H <sub>2</sub> O	(35)	84	[62]
7	Pd/Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	Reflux/MW, EtOH	(30)	99.7	[63]
8	MNP@PAMPS-Pd(II)	80 °C/EtOH-H <sub>2</sub> O	(30)	99	This work
	He +	B(OH) <sub>2</sub> MNP@PAMPS-Pd( K <sub>2</sub> CO <sub>3</sub> EtOH:H <sub>2</sub> O (1:1)	II)		
9	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> -Pd	110 °C/DMF-H <sub>2</sub> O	2	90	[64]
10	rGO/Pd (0.5)	60 °C/EtOH-H <sub>2</sub> O	1(30)	71	[65]
11	Chitosan-supported Pd	50 °C/MW, solvent-free	(4)	64	[66]
12	CL-St-Pd	CL-St-Pd	(6)	59	[67]
13	MNP@PAMPS-Pd(II)	80 °C/EtOH–H <sub>2</sub> O	(45)	90	This work

## 3.4 | Recyclability of MNP@PAMPS-Pd(II)

The reusability of the MNP@PAMPS-Pd(II) catalyst was investigated under the optimized conditions for the

Suzuki–Miyaura reaction of iodobenzene with phenylboronic acid as the model reaction. The catalyst after the first cycle of the reaction was simply taken out with a permanent magnet and washed several times with TABLE 6 Comparison of results using MNP@PAMPS-Pd(II) with those obtained using other catalysts for the Mizoroki-Heck reaction

Entry	Catalyst	Conditions	Time (h (min))	Yield (%)	Ref.
		MNP@PAMPS-Pd(II)	COOMe		
	I + V COOMe	K <sub>2</sub> CO <sub>3</sub> DMF			
1	Thiophene-based iminopyridyl Pd(II) complexes	110 °C/DMF	8	69	[68]
2	[Pd(1-tritylimidazole) <sub>2</sub> Cl <sub>2</sub> ]	110 °C/DMF	12	95	[69]
3	[Pd-BOX-Si] <sup>a</sup>	80 °C/DMF-H <sub>2</sub> O	6	91	[70]
4	Pd/CoBDC	100 °C/DMA	9	95	[71]
5	Pd/CoBDCNH <sub>2</sub>	100 °C/DMA	9	99	[71]
6	Pd@ZPGly <sup>b</sup>	120 °C/aq. CH <sub>3</sub> CN 84%	3	99	[72]
7	MNP@PAMPS-Pd(II)	100 °C/DMF	(40)	98	This work
	Br + COOBu	MNP@PAMPS-Pd(II) K <sub>2</sub> CO <sub>3</sub> DMF	/СООВи		
8	Pd-ATBA-MNPs	120 °C/PEG	8(20)	86	[59]
9	Pd(0)-ABA-Fe <sub>3</sub> O <sub>4</sub>	120 °C/DMF	1(30)	95	[73]
10	Fe <sub>3</sub> O <sub>4</sub> @CS-Schiff base Pd	120 °C/DMF	4	60	[74]
11	ZrO <sub>2</sub> @ECP-Pd	120 °C/[bmim]PF <sub>6</sub>	3	75	[75]
12	MNP@PAMPS-Pd(II)	100 °C/DMF	(45)	94	This work

<sup>a</sup>Silica-supported palladium-bis(oxazoline).

<sup>b</sup>Palladium nanoparticles on zirconium carboxyaminophosphonate nanosheets.

deionized water and ethanol, dried in an oven at 60 °C and reused for further catalytic cycles directly. As can be seen from Figure 9, the catalyst maintained its activity with no significant decrease in the yield up to six runs. Loss of the catalyst during washing could be a reason for the slight decrease of the yield. Changes in the chemical structure of the recycled catalyst were investigated using FT-IR spectroscopy, FE-SEM and EDX analysis. Figure 10 shows the FT-IR spectra of MNP@PAMPS-Pd(II) before and after the catalyst was used six times in the reaction medium. As seen in Figure 10, no significant change in the FT-IR spectrum of the catalyst was observed after six cycles. Moreover, using FE-SEM (Figure 11), the character of the recovered catalyst was determined suggesting that the catalyst remained intact and there was no change in the morphology during the reaction and recycling stages as compared to the pristine catalyst. In addition, the elemental composition (Figure 12) shows the presence of C, N, O, S, Fe and Pd in the nanocomposite structure. The content of palladium in the recovered catalyst was determined as 7.67% (based on EDX results).

13 of 16

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**FIGURE 9** Recyclability of MNP@PAMPS-Pd(II) for Suzuki-Miyaura reaction of iodobenzene with phenylboronic acid (reaction conditions: iodobenzene (1.0 mmol), phenylboronic acid (1.2 mmol),  $K_2CO_3$  (3 mmol), catalyst (5 mg) and EtOH-H<sub>2</sub>O (1:1) (5 ml), at 80 °C)



**FIGURE 10** FT-IR spectra of MNP@PAMPS-Pd(II) (a) before use and (b) after being reused six times

14 of 16 WILEY-Organometallic Chemistry



FIGURE 11 FE-SEM images of MNP@PAMPS-Pd(II) (a) before use and (b) after being reused six times



FIGURE 12 EDX spectrum of recovered MNP@PAMPS-Pd(II)

## 3.5 | Mercury Poisoning Experiments

The most commonly accepted method of assessing catalytic nature (heterogeneous or homogeneous) is the mercury poisoning test.<sup>[22]</sup> If a catalyst is heterogeneous, the most important factor is the surface. If the surface of the catalyst is blocked, no reaction will occur. So, if the catalytic activity is stopped by adding mercury, the catalyst has a heterogeneous nature. But a homogeneous catalyst is not affected by the presence of mercury.<sup>[50]</sup> The results showed that the catalyst was poisoned and lost its activity upon addition of mercury, indicating that the reaction mechanism had a heterogeneous nature (Table 2, entry 7).

## 3.6 | Leaching

To determine the amount of palladium leaching, another catalytic experiment was carried out. For this purpose, the reaction between iodobenzene and phenylboronic acid was performed under the optimized conditions, and the MNP@PAMPS-Pd(II) catalyst was entirely removed from the reaction mixture using an external magnet at approximately 50% conversion of the starting material (15 min). Then, the reaction was allowed to stir for 2 h (and no fresh catalyst was added) and no further reaction and increase in the product yield occurred (monitored by TLC), which is consistent with the heterogeneous nature of the catalyst.<sup>[50]</sup>

## 4 | CONCLUSIONS

- 1. The present work contributes to the development of a novel effective magnetic polymer-supported Pd(II) catalyst.
- 2. The synthesis of PAMPS-grafted modified MNPs with a core-shell structure through a 'grafting from' approach was performed for the first time, and they were effectively employed as a scaffold for immobilizing palladium acetate.
- 3. PAMPS acted as a bidentate ligand, through oxygen and nitrogen atoms, so no additional ligand was added.
- 4. The supported catalyst was confirmed using several analytical techniques including FT-IR spectroscopy, XRD, TGA, TEM, VSM, FE-SEM, ICP-OES and EDX analysis.
- 5. Leaching and mercury tests confirmed the lack of metal leaching and the heterogeneity of the catalyst, respectively.
- 6. Simple catalyst preparation, easy magnetic recyclability and reusability, reusable several times without loss

of activity and high thermal stability are some of the advantages of the protocol presented.

7. The resulting catalyst proved to be a highly efficient heterogeneous catalyst for the Mizoroki–Heck and Suzuki–Miyaura reactions affording excellent yields and remarkable TONs and TOFs. The methodology developed for the mentioned reactions was cost-effective, eco-friendly and simple.

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Applied Organometallic 15 of 16 Chemistry

#### 16 of 16 WILEY-Organometallic Chemistry

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