Palladium-coated thiourea core-shell nanocomposite as a new, efficient, and magnetic responsive nanocatalyst for the Suzuki-Miyaura coupling reactions

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Abstract

In this research, according to the important aspects of palladium components in conducting Suzuki-Miyaura coupling reactions and formation of biphenyl compounds, magnetic responsive palladium/thiourea nanocomposite as a new magnetic nanocatalyst was designed, synthesized, and characterized using FT-IR, EDX, FE-SEM, and VSM analyses. The catalytic performance of this new nanocomposite with magnetic susceptibility was evaluated in the Suzuki-Miyaura coupling reaction. Based on the functionalized surface of Fe3O4 magnetic cores with SiO2, CPTMS, thiourea shells, and especially Palladium ions shell, the formation of biphenyl derivatives in a green and eco-friendly reaction condition was highlighted.

1. Introduction

Thiocarbamide as an organo-sulfur compound with structural similarity to urea, is the alternate name of thiourea. Four elements including nitrogen (36.81%), sulfur (42.11%), carbon (15.77%) and hydrogen (5.31%) are formed the structure of thiourea. The properties of thiourea are substantially distinguished and different from urea due to the oxygen replacement by sulfur atom (Wahid et al. 2017). In comparison to urea, thiourea molecules possess unique features. Their high basicity and considerable polarizability have been converted these molecules to potent nucleophiles in different chemical conditions. Given the quantitative studies on the nucleophilicity of thiourea, it has been indicated that the thione group of thiourea can easily react with wide range of substances such as alkyl halides, aromatic compounds and acylation agents (Mitchell and Steventon 1994). Besides, the chemical efficiency of thiourea has been approved in different fields such as pharmacology and medicinal chemistry, agriculture, industry, and other scientific fields (Sun et al. 2003, Shakeel et al. 2016, An et al. 2018). For instance, thiourea and its derivatives can be utilized as an antioxidant and radioprotective agents owning to its thione-thiol nature (Mitchell and Steventon 1994, Sudzhaev et al. 2011, Sudhamani et al. 2015). Also, thiourea itself can be applied as a plant growth stimulator (Mitchell and Steventon 1994). Apart from these biological applications, various functionalized-thiourea compounds as biosorbent have been reported for removing heavy and toxic metal ions such as Hg(II) (Zhu et al. 2015, Zhou et al. 2017, An et al. 2018), Cr(II) (Liu et al. 2016), Cd(II) (Liu et al. 2016, Yang et al. 2018), Cu(II) (Yang et al. 2018), and Pb(II) (Zhu et al. 2015, Liu et al. 2016, An et al. 2018, Yang et al. 2018). Recently, the focus on thiourea-based organocatalysts has been increased due to their high catalytic capacity and accelerating stereoselective (Andrés et al. 2018) and enantioselective chemical reactions such as Michael addition (Adam et al. 2018, Yao et al. 2018, Yuan et al. 2018), intramolecular Rauhut-Currier reaction (Li et al. 2018a), addition of acetone to nitroalkene (Huang and Jacobsen 2006) and other chemical reactions including asymmetric aldol reactions.
(Takemoto 2010, Heravi et al 2017) and transfer hydrogenation (Qiao et al 2014). Furthermore, thiourea and its derivatives are capable to play the role of systematic ligand in conducting the organometallic reactions (Li et al 2014). Currently, according to the importance of various biological molecules (Esmati et al 2015) and organic compounds (Aghabozorg et al 2011, Foroughian et al 2011, Foroughian et al 2012) in different scientific fields such as pharmacology and biomedicine, transition-metal-catalyzed organic reactions have been created a new research gate for scientists. In these reactions, the most important role of catalytic cycle is conducted by the related transition metal. Also, in order to extend new methodologies, the systematic ligand modulation is required essentially (Li et al 2014). In this regard, one of the most applicable organometallic reactions in the formation of C-C bonds is Suzuki-Miyaura coupling reaction. So far, various catalysts such as [Pd(C₅H₅)₂Cl]₂, Tedicyp (Kondolff et al 2004), Pd[N,N-dimethyl β-alaninate]₂ (Cui et al 2007), [PdBr₂{2,6-[(Ph₂P=O)₂]C₅H₄}] (Kumaravel et al 2014), guanidine/Pd(OAc)₂ (Li et al 2007), β-diketiminatophosphane Pd complex (Lee and Jin 2010), gold nanoparticles (Han et al 2009) or even palladium (Mandal and Chand 2013), complexes of palladium (II), and functionalized palladium nanoparticles (Hajipour et al 2014) have been applied in the synthesis of substituted biphenyl derivatives. However, their catalytic efficiency application can be restricted due to their difficult separation from the reaction media and their recycling process (Maleki et al 2017). In this context, as a solution, the design and fabrication of new heterogeneous magnetic responsive nanocatalysts with substantial features such as ease of surface functionalization, an efficient selectivity, having a large surface to volume ratio, having easy separation and recycling processes by owning magnetic properties can generate a better catalytic condition in the organic reactions (Hajizadeh et al 2019, Ashgharnasl et al 2020, Eivazzadeh-Keihan et al 2020b), especially in Suzuki coupling reaction (Ghorbani-Vaghei et al 2016, Sun et al 2017). Apart from the catalytic activity, wide range of magnetic responsive nanocomposites based on Fe₃O₄ magnetic nanoparticles (Fe₃O₄ MNPs) as core of structure have been reported in different biomedical fields. For instance, various optical and electrochemical biosensors based on Fe₃O₄ MNPs have been synthesized to characterize cancer biomarkers (Eivazzadeh-Keihan et al 2018b, Mohammadinejad et al 2020), neurotoxic proteins, (Eivazzadeh-Keihan et al 2018a), pathogenic viruses (Eivazzadeh-Keihan et al 2019b), and harmful mycotoxins (Eivazzadeh-Keihan et al 2017). Besides, the efficient bio performance of Fe₃O₄-based nanocomposites have been studied in tissue engineering (Eivazzadeh-Keihan et al 2019a), and in-vitro hyperthermia treatment (Bani et al 2019). According to the synthesis importance of substituted biphenyl compounds and fundamental role of palladium in Suzuki-Miyaura coupling reaction, the synthesis process of magnetic responsive palladium/thiourea nanocomposite is introduced in four steps. As can be seen in scheme 1, after surface functionalization of Fe₃O₄ MNPs with inorganic and organic layers such as tetraethyl orthosilicate (TEOS), (3-chloropropyl)-trimethoxysilane (CPTMS) and thiourea, the coordinate interaction of palladium ions coating on the surface of functionalized Fe₃O₄ MNPs is conducted by thiourea molecules which play the role of capping agents. Therefore, at the same time, this synthesized magnetic responsive nanocomposite can demonstrate the magnetic features of Fe₃O₄ MNPs and fundamental catalytic efficiency of palladium ions as coupling agents. Based on the recent progressions in novel methodologies and their accordance with green chemistry principles, the application of magnetic responsive Palladium/thiourea nanocomposite as eco-friendly magnetic nanocatalyst is evaluated in the synthesis of substituted biphenyl derivatives (3a-i) by applying the different substituted aryl halides (1) and substituted boric acids (2) in the presence of potassium carbonate and a combination of two green and nontoxic solvents (water/ethanol) at room temperature condition (scheme 1).

2. Experimental

2.1. General
All the chemical compounds including ingredients and solvents without further purification were purchased from Merck, Fluka and Sigma-Aldrich, the international and chemical companies. FT-IR spectrum of each synthesis step of magnetic responsive nanocomposite was recorded on Shimadzu IR-470 spectrometer (Japan) by the method of KBr pellets. 1H NMR spectra of isolated products were taken with a Bruker DRX-500 Avance spectrometer (Germany) at 500 MHz. The morphology and structure of designed magnetic responsive nanocatalyst was determined by Field-emission scanning microscope (ZEISS-Sigma VP model, Germany) (FE-SEM). Energy-dispersive x-ray (EDX) analysis was taken by using a Numerix DXP-X10P (France) and as well as, the vibrating–sample magnetometer (VSM) analysis was carried out by LBKFB model-magnetic Kavir (Iran). By comparing the spectroscopic and analytical data of authentic samples, isolated products were identified.

2.2. Fabrication procedure of Fe₃O₄ MNPs
Synthesis process of Fe₃O₄ MNPs was carried out by co-precipitation method and doing the following steps (Eivazzadeh-Keihan et al 2019c, Eivazzadeh-Keihan et al 2020a). First, 1.33 g of FeCl₂.4H₂O and 2.91 g of
FeCl₃.6H₂O salt powders (with molar ratio of 2:1) were dissolved in 40 ml of distilled water. Then, the mixture solution was kept under the N₂ atmosphere and mechanical stirring condition by continuous heating up to 70 °C. Afterwards, by considering 30 min, 10 ml of 25% aqueous ammonia solution was added drop wisely to the mixture solution in a stable temperature condition (70 °C). Mechanically, the mixture was stirred for 2 h in a constant temperature condition (70 °C). Finally, after the mentioned time, the black precipitates of synthesized Fe₃O₄ MNPs were separated from the reaction media using an external magnet. Then, to remove unreacted components and reaching to the neural pH (pH = 7), the black precipitates were eluted with distilled water for several times and dried in an oven (70 °C) for an overnight.

2.3. Preparation of Fe₃O₄ MNPs coated by silica layer (Fe₃O₄/SiO₂)
According to the previous studies with some modifications (Stöber et al 1968, Pedroza et al 2005, Pereira et al 2006, Sartoratto et al 2007, De Almeida et al 2010, Eivazzadeh-Keihan et al 2020a), the preparation of Fe₃O₄/SiO₂ nanostructures was conducted by these following steps. First, 0.22 g of Fe₃O₄ MNPs were dispersed into the 50 ml of deionized water by ultrasonic irradiations for 20 min. Then, 7.5 ml of 25% ammonia solution was added drop wisely to the mixture solution under the mechanical stirring condition. After addition of ammonia solution, 80 ml of ethanol was poured into the mixture. In the next step, 4 ml of TEOS solution was drop wisely added to the suspension. The suspension solution was kept stirred mechanically for 24 h at room temperature. Finally, the functionalized nanoparticles were collected by an external magnet and washed with ethanol and deionized water and dried in an oven (70 °C) for an overnight.
2.4. Preparation of SiO$_2$ layered Fe$_3$O$_4$ MNPs coated by CPTMS (Fe$_3$O$_4$/SiO$_2$-Cl)

The placement of second layer, CPTMS molecules, on the surface of functionalized Fe$_3$O$_4$ MNPs were carried out by these following steps. First, 100 ml of dry toluene was added to the 0.69 g of SiO$_2$/Fe$_3$O$_4$ powder at 60 °C under the stirring condition. After few minutes, 1 ml of CPTMS was drop wisely added to the mixture solution. Then, the mixture solution was kept at mentioned temperature and condition for 18 h. Eventually, the elution process of chloropropyl functionalized solid was conducted by dry toluene. The obtained magnetic responsive solid was separated and dried in the vacuum oven for 12 h.

2.5. Functionalization process of modified Fe$_3$O$_4$ MNPs by thiourea (Fe$_3$O$_4$/SiO$_2$-thiourea)

To conduct the third surface functionalization process and placement of thiourea molecules on the surface of modified Fe$_3$O$_4$ MNPs (Fe$_3$O$_4$/SiO$_2$-Cl), first, 0.134 g of functionalized Fe$_3$O$_4$ MNPs were dispersed in 30 ml ethanol. Subsequently, 0.08 g of thiourea powder was added to the intended solution. The mixture solution was kept under the reflux condition for 24 h. After the mentioned time, the obtained product was separated and washed with ethanol for several times. Following that, the functionalized magnetic product was dried in the oven at 70 °C for 12 h.

2.6. Palladium coating procedure on the surface of functionalized Fe$_3$O$_4$ MNPs (Fe$_3$O$_4$/SiO$_2$-thiourea)

The coating process of palladium layer on the surface of functionalized Fe$_3$O$_4$ MNPs (Fe$_3$O$_4$/SiO$_2$-thiourea) was carried out by these following steps. First, in a typical route, 0.11 g of functionalized Fe$_3$O$_4$ MNPs was dispersed in 30 ml of ethanol. Then, 0.025 g of palladium (II) acetate was added to the solution and the mixture was stirred under the reflux condition for 24 h. After the mentioned time, in order to remove the unreacted substances, the elution process was conducted for several times using ethanol. Finally, the obtained magnetic responsive product was dried in the oven (70 °C) for 12 h.

2.7. General process for the synthesis of biphenyl derivatives (3a-i) using Suzuki-Miyaura coupling reaction

Taking into account the room temperature condition, the Suzuki-Miyaura coupling reaction was accomplished in two green solvents (ethanol and water) with miscibility property, applying different kinds of substituted aryl halide (0.5 mmol), substituted phenylboronic acid (0.5 mmol), potassium carbonate (1.5 mmol) and using palladium/thiourea nanocomposite (0.004 g) as synthetic magnetic responsive nanocatalyst. In order to monitor the Suzuki-Miyaura coupling reaction, the progression and completion of reaction was accomplished by TLC (ethyl acetate/n-hexane (1:5)) in appropriate times. Taking into account the reaction accomplishment, the synthesized magnetic responsive catalytic was separated from the reaction media using external magnet. As well as, the substituted biphenyl derivatives were attained by column chromatography process.

3. Results and discussion

In this research study, magnetic responsive palladium/thiourea nanocomposite as new magnetic nanocatalyst was designed, synthesized, and evaluated in Suzuki-Miyaura coupling reaction. To synthesize the magnetic responsive palladium/thiourea nanocomposite, first, the synthesis process of Fe$_3$O$_4$ MNPs as core of this new magnetic responsive nanocomposite is needed. As illustrated in scheme 1, surface functionalization processes were carried out on the surface of Fe$_3$O$_4$ MNPs using inorganic and organic linkers in four synthesis steps. By applying different spectroscopic and analytical techniques including FT-IR spectra for characterizing the functional groups, using EDX analysis to detect structural elements, determining the morphology and size of nanostructures by surface imaging (FE-SEM images) and analyzing the saturation magnetization value (Ms) by VSM analysis, the characterization of magnetic responsive palladium/thiourea nanocomposite is discussed respectively.

3.1. Magnetic responsive Palladium/thiourea nanocomposite characterization

3.1.1. FT-IR analysis

Taking into account the surface functionalization processes of Fe$_3$O$_4$ MNPs and formation of magnetic responsive palladium/thiourea nanocomposite, the FT-IR spectrum was taken from each surface functionalization process (figures 1 (a)–(d)). As could be seen in figure 1 (a), the magnetic phase of unmodified Fe$_3$O$_4$ MNPs is characterized by observing an absorption band at 570 cm$^{-1}$ which is related to the Fe-O stretching vibration mode (Ulu et al 2018). The hydroxyl groups on the surface of magnetic cores are assigned by a broad band at region of 3400 cm$^{-1}$ (Villa et al 2016). In figure 1(b), new absorption bands are observed in the fingerprint region due to the surface functionalization of Fe$_3$O$_4$ MNPs using first coating layer, TEOS. As illustrated in figure 1 (b), The symmetric and asymmetric stretching vibration modes of Si-O-Si bond are ascertained to two absorption bands around 1100 cm$^{-1}$ and 800 cm$^{-1}$. As well as, a small absorption band near
479 cm\(^{-1}\) is attributed to the bending vibration mode of Si-O-Si bond (Safaiee et al. 2015, Villa et al. 2016, Farahi et al. 2017). The O-H stretching vibration mode is characterized by the presence of a broad band at the range of 3100 to 3600 cm\(^{-1}\) (Safaiee et al. 2015). Besides, the O-H stretching vibration of Si-OH bond and the twisting vibration mode of the absorbed H-O-H bond from silica shell are determined by a small absorption band around 1637 cm\(^{-1}\) (Safaiee et al. 2015, Villa et al. 2016, Farahi et al. 2017). The FT-IR spectrum of second surface functionalization process using CPTMS molecules are indicated in figure 1(c). In a close and precise investigation, it can be mentioned that the interaction between CPTMS molecules and SiO\(_2\) shell is well conducted due to characterizing two absorption bands around 1410 cm\(^{-1}\) and 2855 cm\(^{-1}\); which are related to the stretching vibration modes of Si-CH\(_2\) and CH\(_2\) bonds (Vieira et al. 2013). The thiourea functionalized process on the surface of functionalized Fe\(_3\)O\(_4\) MNPs is confirmed by the presence of new functional group (figure 1(d)). As indicated in figure 1(d), the stretching vibration mode of C-N bond and the bending vibration mode of N-C-S bond are characterized by observing two absorption bands around 1465 cm\(^{-1}\) and 622 cm\(^{-1}\). Also, a small absorption peak at 1413 cm\(^{-1}\) is ascribed to the C=S asymmetric stretching vibration mode (Trivedi et al. 2015). Apart from these mentioned results, the symmetric stretching vibration mode of C-N bond is observed at 1086 cm\(^{-1}\) which it has overlapped with the symmetric vibration mode of Si-O-Si bond (Trivedi et al. 2015).

3.1.2. EDX analysis
The EDX spectrum and elemental mapping images of magnetic responsive palladium/thiourea nanocomposite is indicated in figures 2–3. As illustrated in figure 2, the existence of two iron peaks is related to the presence of Fe\(_2\)O\(_3\) MNPs. The presence of Silicon, oxygen and carbon peaks are implied to the placement of SiO\(_2\) and CPTMS layers on the surface of Fe\(_2\)O\(_3\) MNPs. Nitrogen and sulfur peaks confirm conducting the reaction between thiourea and second layer, CPTMS. As well as, the carbon peak can be attributed to the presence of third layer, thiourea, on the surface of modified Fe\(_2\)O\(_3\) MNPs. The fourth layer, palladium coating on the surface of functionalized Fe\(_2\)O\(_3\) MNPs is confirmed by presence of two palladium peak in the EDX spectrum. Apart from EDX spectrum, the uniform distribution and as well, the presence of structural elements is well confirmed by elemental mapping images (figure 3).

3.1.3. FE-SEM imaging
As illustrated, the FE-SEM images of magnetic responsive palladium/thiourea nanocomposite is indicated in figure 4. According to the obtained results, the uniform and unique sphere morphology was observed for magnetic responsive palladium/thiourea nanocomposite. On the other side, according to the important aspects of histogram distribution chart of nanoparticles and its complementary data (Aragón et al. 2015), average size of
functionalized Fe$_3$O$_4$ MNPs was estimated between 230 nm to 240 nm. Therefore, it can be concluded that this size increment can be related to the different surface functionalization processes and placement of thiourea and inorganic shells on the surface of Fe$_3$O$_4$ MNPs.

**Figure 2.** EDX spectrum of magnetic responsive palladium/thiourea nanocomposite.

**Figure 3.** Elemental mapping images of magnetic responsive palladium/thiourea nanocomposite.
3.1.4. VSM analysis

Generally, the saturation magnetization value ($M_s$) of magnetic nanostructures can be determined by Vibrating-sample magnetometer. Magnetic properties of functionalized and unfunctionalized magnetic nanostructures can be changed due to the influence of different parameters, such as iron-group crystalline structure, core size, shell thickness, and their interparticle and intraparticle interactions (Wei et al, 2011). The hysteresis loop curves of unmodified Fe$_3$O$_4$ MNPs and magnetic responsive palladium/thiourea nanocomposite is delineated in figure 5. As could be seen, compared to unmodified Fe$_3$O$_4$ MNPs (figure 5(a)) with high saturation magnetization value (76.20 emu g$^{-1}$), the saturation magnetization value of magnetic responsive palladium/thiourea nanocomposite (21.36 emu g$^{-1}$) has decreased (figure 5(b)). According to this considerable reduction in saturation magnetization value, it can be mentioned that the surface functionalization processes including SiO$_2$, CPTMS, thiourea, and palladium coatings have well conducted on the surface of Fe$_3$O$_4$ MNPs. Therefore, subsequently, these coating shells have reduced the magnetic saturation value of Fe$_3$O$_4$ cores.
In order to obtain the best and optimum condition for synthesis of substituted biphenyl products, the coupling reaction of bromobenzene was considered for comparison. In a close and precise investigation reported catalytic studies, the coupling model reaction including bromobenzene, phenylboronic acid, and thiourea nanocatalyst, the coupling reaction was easily carried out at room temperature condition in a mixture of two green and non-toxic solvents, water, and ethanol (entries 1–10). According to the high catalytic activity of magnetic responsive palladium/thiourea nanocatalyst, the coupling reaction was easily carried out at room temperature condition (table 1, entries 1–10). Due to the reported results, it was determined that the best reaction condition could be provided in a mixture of two green and non-toxic solvents, water, and ethanol (table 1, entries 5, 8). As well as, the highest yield efficiency was reported by using 0.004 g of palladium/thiourea magnetic responsive nanocatalyst (table 1, entry 5). Apart from the optimization of catalyst amount, solvent type, and reaction condition with the highest yield efficiency, in a close and precise investigation, different types of bases were examined in order to find the appropriate base with good functionality in the Suzuki-Miyaura coupling reaction (table 1, entries 5, 8–10). As a result, it was indicated that the potassium carbonate could play an impressive role in increasing the yield percentage of substituted biphenyl products (table 1, entry 5).

Taking into account the best and optimized condition for Suzuki-Miyaura coupling reaction, the desired catalytic performance of magnetic responsive palladium/thiourea nanocatalyst was evaluated by wide range of substituted aryl halides and different substituted boric acids. The synthesis of substituted biphenyl compounds (3a–i) was conducted using 0.004 g of magnetic responsive palladium/thiourea nanocatalyst at room temperature, and considering an average reaction time between 5 to 35 min (table 2, entries 1–9).

### Table 1. Optimization of different parameters for model reaction

| Entry | Catalyst (g) | Solvent | Base | Temperature (°C) | Time (min) | Yield (%)a |
|-------|--------------|---------|------|------------------|------------|------------|
| 1     | 0.004        | acetonitrile | K₂CO₃ | R.T.              | 25         | 20         |
| 2     | 0.004        | acetone   | K₂CO₃ | R.T.              | 25         | 68         |
| 3     | 0.004        | dichloromethane | K₂CO₃ | R.T.              | 25         | 70         |
| 4     | 0.003        | water/ethanol | K₂CO₃ | R.T.              | 25         | 80         |
| 5     | 0.004        | water/ethanol | K₂CO₃ | R.T.              | 25         | 85         |
| 6     | 0.005        | water/ethanol | K₂CO₃ | R.T.              | 25         | 85         |
| 7     | 0.006        | water/ethanol | K₂CO₃ | R.T.              | 25         | 82         |
| 8     | 0.004        | water/ethanol | KOH   | R.T.              | 25         | 80         |
| 9     | 0.004        | water/ethanol | NaOH  | R.T.              | 25         | 79         |
| 10    | 0.004        | water/ethanol | triethylamine | R.T.       | 25         | N.R.       |

a Bromobenzene (0.5 mmol), phenylboronic acid (0.5 mmol), K₂CO₃ (1.5 mmol), magnetic responsive nanocatalyst (0.004 g), ethanol/water (2 ml/2 ml), room temperature.

### 3.2. Catalytic evaluation of magnetic responsive palladium/thiourea nanocomposite

#### 3.2.1. Optimization of different parameters in Suzuki-Miyaura coupling reaction

In order to obtain the best and optimum condition for synthesis of substituted biphenyl products, the coupling reaction of bromobenzene (0.5 mmol) and phenylboronic acid (0.5 mmol) was evaluated by different parameters (table 1, entries 1–10). According to the high catalytic activity of magnetic responsive palladium/thiourea nanocatalyst, the coupling reaction was easily carried out at room temperature condition (table 1, entries 1–10). As well as, the highest yield efficiency was reported by using 0.004 g of palladium/thiourea magnetic responsive nanocatalyst (table 1, entry 5).

#### 3.2.2. Catalytic evaluation of magnetic responsive palladium/thiourea nanocomposite compared to other reported catalysts in Suzuki-Miyaura coupling reaction

In order to compare the catalytic activity of magnetic responsive palladium/thiourea nanocomposite with other reported catalytic studies, the coupling model reaction including bromobenzene, phenylboronic acid, and potassium carbonate was conducted using 0.004 g of magnetic responsive palladium/thiourea magnetic responsive nanocatalyst at room temperature, and considering an average reaction time between 5 to 35 min (table 2, entries 1–9).

#### 3.2.3. Catalytic performance of magnetic responsive palladium/thiourea nanocatalyst in mechanism study of Suzuki-Miyaura coupling reaction

Taking into account the schematic outline of Suzuki-Miyaura coupling reaction in reported literatures (Veisi et al 2014, Zhang and Wang 2015), and due to the high catalytic activity of magnetic responsive palladium/thiourea nanocomposite, the mechanism of Suzuki-Miyaura coupling reaction is proposed. As could be seen in the scheme 2, the process of coupling reaction is initiated with dissolving the chemical ingredient, reduction of Pd²⁺ to Pd⁰ using ethanol cosolvent (Li et al 2007), and forming the intermediate (I). In the oxidative addition process as second step, the organopalladium intermediate (II) is fabricated on the surface of magnetic responsive nanocatalyst due to the aryl halide entrance to the process of coupling reaction. Then, the third step as transmetalation process is carried out in the presence of phenylboronic acid and the organopalladium intermediate (III) is formed. In the last step, the substituted biphenyl derivatives are fabricated and released by reductive
elimination process of Pd$^{2+}$ to Pd$^{0}$. After the reaction completion, the magnetic responsive nanocatalyst is separated from the reaction media using the external magnet. This magnetic catalyst can be utilized for several runs due to its high catalytic capacity.

Table 2. Synthesis of 1,1'-biphenyl derivatives using magnetic responsive palladium/thiourea nanocatalyst.

| Entry | Product     | Time (min) | Yield$^{(\%)}$ |
|-------|-------------|------------|----------------|
| 1     | ![Product](image1) | 25         | 85             |
| 2     | ![Product](image2) | 20         | 87             |
| 3     | ![Product](image3) | 30         | 80             |
| 4     | ![Product](image4) | 35         | 79             |
| 5     | ![Product](image5) | 35         | 84             |
| 6     | ![Product](image6) | 35         | 75             |
| 7     | ![Product](image7) | 5          | 93             |
| 8     | ![Product](image8) | 5          | 95             |
| 9     | ![Product](image9) | 5          | 90             |

$^{(a)}$ Isolated yield.
| Entry | Catalyst Description | Amount of Catalyst | Base | Solvent | Temp. (°C) | Time (min) | Yield (%) | References |
|-------|----------------------|--------------------|------|---------|-----------|------------|-----------|------------|
| 1     | Biothiol-tempelated Pd NPs | 0.03 (mol%) | KOH | EtOH/H₂O | 60 | 60 | 54.28 | (Li et al. 2018b) |
| 2     | Pd/Fe₃O₄/ZnO | 0.003 (g) | K₂CO₃ | H₂O | 100 | 180 | 70 | (Hosseini-Sarvari et al. 2016) |
| 3     | Ni/Pd core/shell NPs | 0.01 (g) | K₂CO₃ | DMF/H₂O | 110 | 30 | 78 | (Metin et al. 2013) |
| 4     | Palladium complex | 0.1 (mol%) | K₂CO₃ | DMF | 120 | 720 | 80 | (Trivedi et al. 2016) |
| 5     | GO-2N-Pd(II) | 0.5 (mol%) | K₂CO₃ | EtOH | 80 | 240 | 82 | (Bai et al. 2014) |
| 6     | Palladium/thiourea nanocomposite | 0.004 (g) | K₂CO₃ | EtOH/H₂O | R.T. | 25 | 85 | Present study |

* Isolated yield.
3.2.4. Catalytic reusability of magnetic responsive palladium/thiourea nanocomposite for several runs

Having high catalytic capacity and reusability are two crucial factors in designing high potent and stable catalysts. Taking into account these features, the recovery process of wide ranges of magnetic responsive nanocomposite is conducted in order to estimate their catalytic capacity. For this purpose, the magnetic responsive palladium thiourea nanocatalyst was separated from the reaction media using an external magnet.
 Afterwards, the elution process of this synthesized magnetic responsive nanocatalyst was carried out by ethanol, the green and non-toxic solvent. After dilution process, it was kept in the oven at 70 °C for an overnight. The catalytic capacity and recycle-ability of magnetic responsive palladium/thiourea nanocatalyst were evaluated by its reusing in coupling model reaction. Based on the obtained results, no substantial reduction was observed in its catalytic efficiency after 5 runs (scheme 2). Therefore, it can be mentioned that this new magnetic responsive nanocatalyst has its high catalytic capacity and recycle-ability (Supplementary information, figures S2–S3 (available online at stacks.iop.org/MRX/8/026102/mmedia)).

4. Conclusions

As a summary, in this research study, new magnetic responsive palladium/thiourea nanocomposite with excellent catalytic activity and magnetic susceptibility was designed and synthesized. FT-IR, EDX, FE-SEM, and VSM analyses were used to characterized its structural features such as formation of new functional groups, its structural elements, unique sphere morphology, and excellent magnetic property. The surface of Fe3O4 MNPs as a core of this new magnetic nanocatalyst are functionalized with different inorganic and organic shells in four synthesis steps. Apart from SiO2, CPTMS, and thiourea shells, in fact, the coordination interaction of palladium ions and thiourea molecules can facilitate the Suzuki-Miyaura coupling reaction and formation of biphenyl products. Following the catalytic activity, its substantial stability and recycle ability was evaluated five times. In spite of five catalytic runs and recycling process, the catalytic capacity of magnetic responsive palladium/thiourea nanocomposite was considerable and no particular reduction was observed in the isolated yield percentage of obtained products.

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Data availability statement

Competing interest statement

The authors whose names are listed in this article have no conflict of interests in this paper.

Authors’ contributions

A M has designed the study, managed the project, analysis and characterization, and participated in discussing of the results. R E and N B has carried out the literature study, performed the analyses, conducted the optimization, purification of the compounds and prepared the draft of the manuscript. F R has edited and revised the manuscript. All authors read and approved the final manuscript.

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