Pd@Py2PZ@MSN as a Novel and Efficient Catalyst for C-C Bond Formation Reactions

Mohammad Hossein Sayahi (sayahymh@pnu.ac.ir)
Payame Noor University (PNU)

Mansoureh Toosibashi
University of Tehran

Mehdi Bahmaei
Payame Noor University (PNU)

Hosein Lijan
University of Tehran

Leila Malimani
Agricultural Biotechnology Research Institute of Iran (ABRII), Agricultural Research Education and Extension Organization (AREEO)

Mohammad Mahdavi
Tehran University of Medical Sciences

Saeed Bahadorikhalili
Tehran University of Medical Sciences

Research Article

Keywords: Palladium catalyst, immobilized catalyst, mesoporous silica nanoparticles, Heck reaction, Suziki reaction.

DOI: https://doi.org/10.21203/rs.3.rs-661021/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License
Abstract

In this paper, a novel catalyst is introduced based on the immobilization of palladium onto dipyrido[3,2-a:2',3'-c]phenazine modified mesoporous silica nanoparticles. Dipyrido[3,2-a:2',3'-c]phenazine (Py₂PZ) ligand is synthesized in a simple method from the reaction of 1,10-phenanthroline-5,6-dione and 3,4-diaminobenzoic acid as starting materials. The ligand is used to functionalize mesoporous silica nanoparticles (MSN) and to modify its surface chemistry for immobilization of palladium. The palladium immobilized dipyrido[3,2-a:2',3'-c]phenazine modified mesoporous silica nanoparticles (Pd@Py₂PZ@MSN) are synthesized and characterized by several characterization techniques, including TEM, SEM, FTIR, TGA, ICP, XRD, and EDS analysis. After the careful characterization of Pd@Py₂PZ@MSN, the activity and efficiency of this catalyst is examined in carbon-carbon bond formation reactions. The results are advantageous in water and the products are obtained in high isolated yields. In addition, the catalyst shows very good reusability and did not show significant loss in activity after 10 sequential runs.

Introduction

Carbon-carbon bond formation reactions, especially palladium catalyzed ones, are of significant reactions in organic chemistry. Among all the palladium catalyzed carbon-carbon bond formation reactions, Heck and Suzuki reactions have attracted interests, due to their high applications in various organic synthesis. Regarding the unique advantages of Heck and Suzuki reactions, these reactions are used for the synthesis of several compounds with complex chemical structures. Therefore, several efforts have been focused on the introduction of novel catalysts with improved characteristics.

An interesting approach for designing of novel catalysts for Heck and Suzuki reactions is the immobilization of palladium onto modified nanoparticles. This method, enables both the advantages of homogeneous and heterogeneous catalysts. Several nanoparticles including nanosilica, nitrogen rich polymers, chitosan, magnetic iron oxide, and graphene oxide have been used as support for palladium catalysts. Mesoporous silica nanoparticles (MSN) is an interesting ordered porous material, made of silica with high surface area and unique physical and chemical properties. MSN is chemically and physically stable and is compatible to biological systems. MSNs have been used in various applications, including catalysis, drug delivery, tissue engineering, and pollutant removal from air and solutions. Based on the high surface area and stability and the ease of the functionalization of MSN, this family of nanoporous materials has expensively used as support for catalysts in various reactions.

In this study, we introduce a novel palladium catalyst supported onto dipyrido[3,2-a:2',3'-c]phenazine modified MSN. The catalytic activity of Pd@Py₂PZ@MSN is evaluated in Heck and Suzuki reactions.

Results And Discussion
In this paper, SBA-15 MSN was synthesized by hydrothermal method and modified by (3-aminopropyl)methoxysilane. Dipyrido[3,2-a:2',3'-c]phenazine (Py$_2$PZ) was synthesized in one step reaction between 3,4-diaminobenzoic acid and 1,10-phenanthroline-5,6-dione, which enables to react with amine groups on the surface of MSN via an amidation reaction to give Py$_2$PZ@MSN. Pd@Py$_2$PZ@MSN catalyst was prepared using Py$_2$PZ@MSN as a support and it was fully characterized by various characterization techniques. The synthesis steps are presented in Scheme 1.

Electron microscopy images of Pd@Py$_2$PZ@MSN catalyst are shown in Fig. 1. The hexagonal mesostructure of MSN-backbone could be observed in TEM image that Pd NPs appear as the dark zones (Fig. 1a). The rod like structure of MSN could clearly be observed in SEM image (Fig. 1b). In addition, EDS analysis of Pd@Py$_2$PZ@MSN catalyst confirms the presence of Pd in the structure of the catalyst (Fig. 1c). As seen in Fig. 1d, XRD pattern of Pd@Py$_2$PZ@MSN catalyst confirms that the crystallinity of the catalyst is similar to SBA-15$^{38}$. In addition, the high angle XRD confirms the presence of Pd NPs by two peaks of 110 and 200 planes at 2θ of 39.2 and 44.3 degrees, respectively (Fig. 1d).

To confirm the successful synthesis of Pd@Py$_2$PZ@MSN, the FT-IR spectra of nanomaterials was compared (Fig. 2a). In the FT-IR spectra of Pd@Py$_2$PZ@MSN, a peak at 1084 cm$^{-1}$ represents Si-O vibrations in the structure of the catalyst. Hydroxyl groups of the catalyst could be observed at 3450 cm$^{-1}$ and the CH$_2$ stretching vibration are presented at 2927 cm$^{-1}$. The peak appeared at 1739 cm$^{-1}$ is attributed to the C = O bond found in the ester moiety in the structure of Pd@Py$_2$PZ@MSN catalyst.

The organic content in the structure of the catalyst was studied by TGA analysis (Fig. 2b). TGA curve shows that the catalyst was thermally stable up to 250°C. A weight loss at temperature of 250–350°C could be observed, which could be correlated to the degradation of organic moieties in the structure of Pd@Py$_2$PZ@MSN catalyst. The palladium content in the structure of the catalyst was measured by ICP analysis. The results showed the Pd content in Pd@Py$_2$PZ@MSN catalyst was 0.12 mmol.g$^{-1}$.

The surface area and the pore size of Pd@Py$_2$PZ@MSN catalyst was characterized by BET analysis and compared with MSN nanoparticles. Based on the BET and nitrogen adsorption-desorption results, Py$_2$PZ@MSN has a high surface area of 612.37 m$^2$.g$^{-1}$. In addition, the pore diameter and pore volume of the synthesized nanoporous support are 5.14 nm and 0.72 cm$^3$.g$^{-1}$, respectively. Surface area, pore width and pore volumes of MSN are 655.37 m$^2$.g$^{-1}$, 5.75 nm, and 0.79 cm$^3$.g$^{-1}$, respectively. The decrease in surface area, pore width and pore volume of MSN by the synthesis of the catalyst is expected, while functionalization of the nanoparticles leads to such changes. The surface area and pore size results of MSN and Pd@Py$_2$PZ@MSN catalyst are presented in Table 1.
Table 1
Surface area and pore size results of MSN and Pd@Py₂PZ@MSN catalyst.

|                  | Surface area (m².g⁻¹) | Pore width (nm) | Pore volume (cm³.g⁻¹) |
|------------------|-----------------------|-----------------|-----------------------|
| MSN              | 655.65                | 5.75            | 0.79                  |
| Pd@Py₂PZ@MSN     | 612.37                | 5.14            | 0.72                  |

After the characterization of Pd@Py₂PZ@MSN catalyst, the efficiency of the catalyst was examined in carbon-carbon bond formation reactions. To this purpose, Pd@Py₂PZ@MSN catalyst was used in Heck and Suzuki reactions. Initially, the optimal reaction conditions were evaluated by performing the reaction under different reaction conditions including various solvents, bases, catalysts and the times of the reactions. To this end, the reaction of styrene and phenyl bromide was selected as a model reaction. The optimization results are presented in Table 2. According to the results, the best solvent for the reaction is water. However, the yields of the product were less in other solvents. Therefore, water was selected as the best solvent for the reaction. In addition, the results showed that the best yield of the product is obtained when the reaction is performed in the presence of 1 mol% of the catalyst. It should be noted that the presence of a base is critical for the reaction performance. Therefore, the reaction was performed in the presence of several bases such as triethyl amine (TEA), NaOH, KOH, and Pyridine. The results showed that TEA was the best base for the reaction. To study the role of Pd@Py₂PZ@MSN catalyst in the reaction, a blank run was performed by all the reaction components except the catalyst. No product was obtained in the absence of the catalyst. Therefore, the optimized reaction conditions were selected to be water as solvent, 1.5 equivalent of triethyl amine base in the presence of 1.0 mol% of Pd@Py₂PZ@MSN catalyst.

To rule out the presence of leached and homogenous Pd in the reaction mixture, in a run, the reaction was performed under the optimal reaction condition. After 60 min, the conversion of the substrates to the product measured by GC was 67%. Then, the catalyst was separated from the reaction mixture and the filtrate was stirred under the same conditions for more 60 min. The analysis of the product by GC showed that no more product has been obtained. These observations confirmed the Pd catalyst worked in the heterogeneous phase and the presence of Pd@Py₂PZ@MSN catalyst was necessary for the reaction performance.
Table 2
Optimization of the reaction of styrene and phenyl bromide in the presence of Pd@Py$_2$PZ@MSN catalyst.

| Entry | Solvent | Base (mol) | Catalyst (mol %) | Time(min) | Yield (%) |
|-------|---------|------------|------------------|-----------|-----------|
| 1     | EtOH    | TEA (1.5)  | Pd@Py$_2$PZ@MSN (1.0) | 120       | 61        |
| 2     | MeOH    | TEA (1.5)  | Pd@Py$_2$PZ@MSN (1.0) | 120       | 67        |
| 3     | CH$_2$Cl$_2$ | TEA (1.5)  | Pd@Py$_2$PZ@MSN (1.0) | 120       | 47        |
| 4     | DMF     | TEA (1.5)  | Pd@Py$_2$PZ@MSN (1.0) | 120       | 59        |
| 5     | H$_2$O  | TEA (1.5)  | Pd@Py$_2$PZ@MSN (1.0) | 120       | 94        |
| 6     | H$_2$O  | NaOH (1.5) | Pd@Py$_2$PZ@MSN (1.0) | 120       | 80        |
| 7     | H$_2$O  | KOH (1.5)  | Pd@Py$_2$PZ@MSN (1.0) | 120       | 87        |
| 8     | H$_2$O  | Pyridine (1.5) | Pd@Py$_2$PZ@MSN (1.0) | 120       | 69        |
| 9     | H$_2$O  | K$_2$CO$_3$ | Pd@Py$_2$PZ@MSN (1.0) | 120       | 77        |
| 10    | H$_2$O  | No base    | Pd@Py$_2$PZ@MSN (1.0) | 120       | Trace     |
| 11    | H$_2$O  | TEA (0.5)  | Pd@Py$_2$PZ@MSN (1.0) | 120       | 55        |
| 12    | H$_2$O  | TEA (1.0)  | Pd@Py$_2$PZ@MSN (1.0) | 120       | 70        |
| 13    | H$_2$O  | TEA (2.0)  | Pd@Py$_2$PZ@MSN (1.0) | 120       | 94        |
| 14    | H$_2$O  | TEA (1.5)  | Pd@Py$_2$PZ@MSN (0.5) | 120       | 46        |
| 15    | H$_2$O  | TEA (1.5)  | Pd@Py$_2$PZ@MSN (1.5) | 120       | 94        |
| 16    | H$_2$O  | TEA (1.5)  | Pd@Py$_2$PZ@MSN (1.0) | 60        | 67        |
| 17    | H$_2$O  | TEA (1.5)  | Pd@Py$_2$PZ@MSN (1.0) | 150       | 94        |
| 18    | H$_2$O  | TEA (1.5)  | Pd/C (1.0)       | 120       | 56        |
| 19    | H$_2$O  | TEA (1.5)  | Pd(OAc)$_2$ (1.0) | "        | 69        |
| 21    | H$_2$O  | TEA (1.5)  | PdCl$_2$ (1.0) | "        | 61        |
| 22    | H$_2$O  | TEA (1.5)  | No catalyst      | "        | 0         |

Reaction conditions: styrene (1 mmol); phenyl bromide (1 mmol); catalyst; solvent (5 mL); base; 25 °C.
Based on the optimized conditions, the scope and the generality of Pd@Py$_2$PZ@MSN catalyst was studied in Heck and Suzuki reactions. The structures and the yields of the products are presented in Table 3. The high efficiency of Pd@Py$_2$PZ@MSN catalyst in the mentioned reaction could clearly be observed. The catalyst is highly active in both Heck and Suzuki reactions and advantageous results were obtained. All substrates with electron donating and electron withdrawing functionalities have gave the desired products in high isolated yields. For example, entries 4–9, 18–22, and 26–28 with phenyl halides bearing electron donating functionalities have given the products in 84–93% yields. In addition, phenyl halides bearing electron withdrawing functionalities (entries 10–14, 22–23, 29–31) have successfully participated in the reaction and have given the products in 88–99% yields. In addition, a reaction was performed with 10 mmol of the substrates to evaluate the possible scale up of the reaction. The results were advantageous and high yields of the products were obtained in the scale up reactions. The large scale reaction of iodobenzene with styrene and phenylboronic acid have led to 85% and 83% yields, respectively.

Table 3. The scope and generality of Pd@Py$_2$PZ@MSN catalyst in Heck and Suzuki reactions

```
R\[X\] + Z \xrightarrow{\text{Pd@Py$_2$PZ@MSN, H$_2$O, r.t.}} \text{R\[Z\]}
```
| Entry | R   | Z            | X    | Time (min) | Yield (%) | TON** | TOF*** |
|-------|-----|--------------|------|------------|-----------|-------|--------|
| 1     | H   | Styrene      | Br   | 120        | 94        | 9400  | 4700   |
| 2     | H   | Styrene      | Cl   | 150        | 79        | 7900  | 3160   |
| 3     | H   | Styrene      | I    | 120        | 96        | 9600  | 4800   |
| 4     | 4-Me| Styrene      | Br   | 120        | 90        | 9000  | 4500   |
| 5     | 4-Me| Styrene      | Cl   | 150        | 75        | 7500  | 3000   |
| 6     | 4-Me| Styrene      | I    | 120        | 94        | 9400  | 4700   |
| 7     | 4-OMe| Styrene     | Br   | 120        | 91        | 9100  | 4550   |
| 8     | 4-OMe| Styrene    | I    | 120        | 93        | 9300  | 4650   |
| 9     | 4-NMe₂| Styrene    | Br   | 120        | 93        | 9300  | 4650   |
| 10    | 4-Cl| Styrene      | Br   | 120        | 96        | 9600  | 4800   |
| 11    | 4-Cl| Styrene      | Cl   | 150        | 70        | 8000  | 3200   |
| 12    | 4-CN| Styrene      | Br   | 120        | 94        | 9400  | 4700   |
| 13    | 4-CN| Styrene      | Cl   | 150        | 78        | 8800  | 3520   |
| 14    | 4-CHO| Styrene    | Br   | 120        | 93        | 9300  | 4650   |
| 15    | H   | butyl acrylate| Br   | 120        | 96        | 9600  | 4800   |
| 16    | H   | butyl acrylate| Cl   | 150        | 82        | 8200  | 3280   |
| 17    | H   | butyl acrylate| I    | 90         | 96        | 9600  | 6400   |
| 18    | 4-Me| butyl acrylate| Br   | 120        | 89        | 8900  | 4450   |
| 19    | 4-Me| butyl acrylate| Cl   | 150        | 75        | 7500  | 3000   |
| 20    | 4-OMe| butyl acrylate| Br   | 120        | 91        | 9100  | 4550   |
| 21    | 4-OMe| butyl acrylate| Cl   | 150        | 76        | 7600  | 3040   |
| 22    | 4-CN| butyl acrylate| Br   | 120        | 94        | 9400  | 4700   |
| 23    | 4-CN| butyl acrylate| Cl   | 150        | 89        | 8900  | 3560   |
| 24    | H   | Ph(BOH)₂      | Br   | 120        | 92        | 9200  | 4600   |

* Reaction conditions: styrene, butyl acrylate, or phenylboronic acid (1 mmol); phenyl halide (1 mmol); Pd@Py₂PZ@MSN catalyst (1 mol%); H₂O (5 mL); TEA (1.5 mmol); 25°C; ** TON is calculated as the number of moles of substrate converted to product divided by the number moles of palladium catalyst; *** TOF is defined as TON h⁻¹; **** Scale up reactions: styrene or phenylboronic acid (10 mmol); phenyl bromide (10 mmol); Pd@Py₂PZ@MSN catalyst (1 mol%); H₂O (50 mL); TEA (15 mmol); 25°C.
| Entry | R    | Z               | X  | Time (min) | Yield (%) | TON** | TOF*** |
|-------|------|-----------------|----|------------|-----------|-------|--------|
| 25    | H    | Ph(BOH)$_2$    | I  | 150        | 97        | 9700  | 3880   |
| 26    | 4-Me | Ph(BOH)$_2$    | Br | 120        | 88        | 8800  | 4400   |
| 27    | 4-Me | Ph(BOH)$_2$    | I  | 150        | 92        | 9200  | 3680   |
| 28    | 4-OMe| Ph(BOH)$_2$    | Br | 120        | 84        | 8400  | 4200   |
| 29    | 4-Cl | Ph(BOH)$_2$    | Br | 120        | 93        | 9300  | 4650   |
| 30    | 4-CN | Ph(BOH)$_2$    | Br | 120        | 95        | 9500  | 4750   |
| 31    | 4-CN | Ph(BOH)$_2$    | I  | 150        | 99        | 9900  | 3960   |
| 32****| H    | Styrene        | I  | 120        | 85        | 8500  | 4250   |
| 33****| H    | Ph(BOH)$_2$    | I  | 120        | 83        | 8300  | 4150   |

* Reaction conditions: styrene, butyl acrylate, or phenylboronic acid (1 mmol); phenyl halide (1 mmol); Pd@Py$_2$PZ@MSN catalyst (1 mol%); H$_2$O (5 mL); TEA (1.5 mmol); 25°C; ** TON is calculated as the number of moles of substrate converted to product divided by the number moles of palladium catalyst; *** TOF is defined as TON h$^{-1}$.; **** Scale up reactions: styrene or phenylboronic acid (10 mmol); phenyl bromide (10 mmol); Pd@Py$_2$PZ@MSN catalyst (1 mol%); H$_2$O (50 mL); TEA (15 mmol); 25°C.

A great advantage of Pd@Py$_2$PZ@MSN catalyst is its reusability. To illustrate the reusability of the catalyst, after the reaction of styrene (or phenylboronic acid) and phenyl bromide was completed, the catalyst was separated by filtration. The separated catalyst was washed, dried, and used in next reaction run under the same reaction conditions. The reaction was repeated for 10 sequential reactions that the obtained results are presented in Fig. 3. It could be seen that in both Heck and Suzuki reactions, no big loss in the activity of the catalyst is observed.

To show the structural stability of the catalyst during the reaction conditions, the catalyst was separated after the 5th reaction run, washed with water and ethanol. Then, the dried 5th re-used Pd@Py$_2$PZ@MSN catalyst was characterized by SEM and BET analysis. The results are presented in Fig. 4 and Table 4, respectively. Comparing the results of the recovered catalyst with the fresh ones confirm the good stability of the catalyst during the reactions.

### Table 4
Surface area and pore size results of the recovered Pd@Py$_2$PZ@MSN catalyst.

| Surface area (m$^2$.g$^{-1}$) | Pore width (nm) | Pore volume (cm$^3$.g$^{-1}$) |
|-------------------------------|-----------------|-----------------------------|
| 607.21                        | 5.09            | 0.70                        |
Experimental

General remarks

All the chemicals, reagents, and solvent were purchased from Merck, Germany and Sigma, Germany. TEM images were recorded on a CM 10 Philips instrument. $^1$H (500 MHz) spectra were recorded on a Bruker Avance spectrometer in DMSO, d$_6$ solution with tetramethylsilane (TMS) as an internal standard. A TESCAN T3000 instrument was applied to record the SEM images. OPTIMA7300DV ICP analyzer was applied for analyzing the palladium content of the catalyst. The FT-IR spectra were recorded on a Nicolet Magna FT-IR 550 spectrophotometer using potassium bromide disks. BET of the samples was analyzed by an ASAPTM micromeritics 2020 instrument. The particle size was measured using HORIBA SZ100-Z DLS instrument. Thermo-gravimetric Analyzer (TGA) at heating rate of 10 °C min$^{-1}$ over the temperature range of 40–600 °C under nitrogen atmosphere.

Synthesis of Py$_2$PZ ligand

1,10-Phenanthroline-5,6-dione (1.05 g, 5 mmol) and 3,4-diaminobenzoic acid (0.76 g, 5 mmol) were dissolved in ethanol and refluxed for 2h. The reaction progress was monitored by TLC monitoring. After the reaction completion, the solvent was evaporated and the product was purified by recrystallization from ethanol.

Synthesis of Pd@Py$_2$PZ@MSN catalyst

SBA-15 was synthesized according to previously reported method $^{39}$. A mixture containing mesoporous silica nanoparticles (0.5 g) in ethanol/deionized water (1:2, 30 mL) and HCl (pH = 4) was prepared and sonicated for 30 min. A solution of (3-aminopropyl) methoxysilane (1 g) in ethanol (30 mL) was prepared and added drop-wise to the above mixture by vigorous stirring. The reaction mixture was stirred for 24 h and then, the product was separated by filtration and washed with deionized water and ethanol. The product was dried at 70 °C in vacuum for 12 h to obtain amine modified mesoporous SBA-15.

A mixture of amine modified mesoporous SBA-15 (0.5 g) in dichloromethane (75 mL) was sonicated for 30 min. Then, dipyrido[3,2-\textit{a}':2',3'-\textit{c}]phenazine-11-carboxylic acid (1.6 g, 5 mmol) in dichloromethane (25 mL), was added of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (5 mmol, 1 eq) and $N$- hydroxysuccinimide (5.5 mmol, 1.1 eq) were added. The reaction mixture was stirred overnight at room temperature. The product was separated from the reaction mixture and washed with ethanol and dried for 12 h in a vacuum oven.

The solid support (0.5 g) was added to dry acetone and sonicated for 30 min. Then, PdCl$_2$ (1 mmol) was added and the reaction mixture was stirred at 40 °C under inert atmosphere for 24 h. Pd@Py$_2$PZ@MSN catalyst, was separated from the reaction mixture by centrifugation, washed thoroughly with EtOH and diethyl ether and dried under vacuum at room temperature for 12 h.
General procedure for the carbon-carbon bond formation reactions

Phenyl halide (1 mmol), alkene (1.1 mmol, in case of Heck reaction), phenyl boronic acid (1.0 mmol, in case of Suzuki reaction), triethyl amine (1.5 mmol) and Pd@Py$_2$PZ@MSN catalyst (1.0 mol%) were added into a flask containing H$_2$O (5 mL) and stirred at room temperature. When the TLC monitoring showed the reaction completion, the catalyst was separated from the reaction mixture and washed with water and EtOH. The product was extracted with ethyl acetate. The organic phase was collected dried over sodium sulfate. Solvent was evaporated and the product was purified using column chromatography using n-hexane:ethyl acetate (6:1) as eluent to obtain pure product.

Recovery of the nanocatalyst

The reaction of phenyl bromide (1 mmol) and styrene (1.1 mmol) was selected as a model reaction and was performed in the presence of Pd@Py$_2$PZ@MSN catalyst under the optimal reaction conditions. After the reaction completion, the catalyst was separated from the reaction mixture and washed with water and used in the next reaction under the same conditions. The reactions were performed for 10 sequential runs.

Conclusion

In conclusion, Pd@Py$_2$PZ@MSN as a novel catalyst was designed, synthesized and characterized based on the immobilization of palladium onto the modified SBA-15 mesoporous silica nanoparticles. The catalyst was characterized by several methods and the structure of the catalyst was confirmed. The activity of Pd@Py$_2$PZ@MSN catalyst was evaluated in Heck and Suzuki reactions. The catalyst showed the best activity in water as solvent in the presence of triethyl amine base. Several substrates with different functionalities were used and, in all cases, the desired compounds were synthesized in good isolated yields. As an advantage, the catalyst showed very good reusability after 10 sequential runs.

Declarations

Conflict of interest

The authors declare no conflict of interest.

References

1. Christoffel, F. & Ward, T. R. Palladium-catalyzed Heck cross-coupling reactions in water: A comprehensive review. Catal. Lett, 148, 489–511 (2018).

2. González-Sebastián, L. & Morales-Morales, D. Cross-coupling reactions catalysed by palladium pincer complexes. A review of recent advances. Journal of Organometallic Chemistry, 893, 39–51 (2019).
3. Mpungose, P. P., Vundla, Z. P., Maguire, G. E. & Friedrich, H. B. The current status of heterogeneous palladium catalysed Heck and Suzuki cross-coupling reactions., 23, 1676 (2018).

4. Bahadorikhalili, S. & Mahdavi, H. Palladium magnetic nanoparticle-polyethersulfone composite membrane as an efficient and versatile catalytic membrane reactor. Polymers for Advanced Technologies, 29, 1138–1149 (2018).

5. Fusini, G. et al. Polyvinylpyridine-Supported Palladium Nanoparticles: An Efficient Catalyst for Suzuki–Miyaura Coupling Reactions. Catalysts, 10, 330 (2020).

6. Tashrifi, Z. et al. Synthesis and characterization of γ-Fe2O3@SiO2–(CH2)3–PDTC–Pd magnetic nanoparticles: a new and highly active catalyst for the Heck/Sonogashira coupling reactions. New Journal of Chemistry, 43, 8930–8938 (2019).

7. Easson, M. W., Jordan, J. H., Bland, J. M., Hinchliffe, D. J. & Condon, B. D. Application of Brown Cotton-Supported Palladium Nanoparticles in Suzuki–Miyaura Cross-Coupling Reactions. ACS Applied Nano Materials, 3, 6304–6309 (2020).

8. Sherwood, J., Clark, J. H., Fairlamb, I. J. & Slattery, J. M. Solvent effects in palladium catalysed cross-coupling reactions. Green Chem, 21, 2164–2213 (2019).

9. Yao, T., Zhang, F., Zhang, J. & Liu, L. Palladium-Catalyzed Intermolecular Heck-Type Dearomative [4 + 2] Annulation of 2 H-Isindoide Derivatives with Internal Alkynes. Org. Lett, 22, 5063–5067 (2020).

10. Zhou, B. et al. Dearomative 1, 4-difunctionalization of naphthalenes via palladium-catalyzed tandem Heck/Suzuki coupling reaction. Nature communications, 11, 1–10 (2020).

11. Bahadorikhalili, S., Mañani, L., Lijan, H. & Mahdavi, M. γ-Fe2O3@SiO2(CH2)3-HPBM-Pd as a Versatile Boosted Nanocatalyst for CarbonCarbon Bond Formation. Materials Today Communications, 101913 (2020).

12. Bahadorikhalili, S. et al. Palladium functionalized phosphinite polyethyleneimine grafted magnetic silica nanoparticles as an efficient catalyst for the synthesis of isoquinolinol[1,2-b]quinazolin-8-ones. New Journal of Chemistry, 42, 5499–5507 (2018).

13. Hajipour, A. R. & Khorsandi, Z. Asymmetric Intermolecular Heck Reaction of Aryl Halides by Pd-histidine Organocatalysts. Modern Chemistry, 8, 18 (2020).

14. Hajipour, A. R., Sadeghi, A. R. & Khorsandi, Z. Pd nanoparticles immobilized on magnetic chitosan as a novel reusable catalyst for green Heck and Suzuki cross-coupling reaction: In water at room temperature. Appl. Organomet. Chem, 32, e4112 (2018).

15. Ma, R., Yang, P. & Bian, F. Magnetic dendritic polymer nanocomposites as supports for palladium: a highly efficient and reusable catalyst for Mizoroki–Heck and Suzuki–Miyaura coupling reactions. New Journal of Chemistry, 42, 4748–4756 (2018).

16. Isfahani, A. L. et al. Palladium nanoparticles immobilized on nano-silica triazine dendritic polymer (Pdnp-nSTDP): An efficient and reusable catalyst for Suzuki–Miyaura cross-coupling and Heck reactions. Adv. Synth. Catal, 355, 957–972 (2013).
17. Khalafi-Nezhad, A. & Panahi, F. Size-controlled synthesis of palladium nanoparticles on a silica–cyclodextrin substrate: A novel palladium catalyst system for the Heck reaction in water. *ACS Sustainable Chemistry & Engineering, 2*, 1177–1186 (2014).

18. Targhan, H., Hassanpour, A., Sohrabnezhad, S. & Bahrami, K. Palladium Nanoparticles Immobilized with Polymer Containing Nitrogen-Based Ligand: A Highly Efficient Catalyst for Suzuki–Miyaura and Mizoroki–Heck Coupling Reactions. *Catal. Lett*, 150, 660–673 (2020).

19. Kumari, S., Layek, S. & Pathak, D. D. Palladium nanoparticles immobilized on a magnetic chitosan-anchored Schiff base: applications in Suzuki–Miyaura and Heck–Mizoroki coupling reactions. *New Journal of Chemistry, 41*, 5595–5604 (2017).

20. Bahadorikhalili, S., Ma’mani, L., Mahdavi, H. & Shafiee, A. Palladium catalyst supported on PEGylated imidazolium based phosphinite ionic liquid-modified magnetic silica core–shell nanoparticles: a worthy and highly water-dispersible catalyst for organic reactions in water. *RSC advances, 5*, 71297–71305 (2015).

21. Ma’mani, L. *et al.* Palladium catalyst supported on N-aminoguanidine functionalized magnetic graphene oxide as a robust water-tolerant and versatile nanocatalyst. *RSC Advances, 4*, 48613–48620 (2014).

22. Kumari, S., Mittal, A., Kumar, A. & Sharma, S. K. Palladium Nanoparticles Immobilized on Schiff Base-Functionalized Graphene-Oxide: Application in Carbon-Carbon Cross-Coupling Reactions. *ChemistrySelect, 4*, 10828–10837 (2019).

23. Mehmood, A., Ghafar, H., Yaqoob, S., Gohar, U. F. & Ahmad, B. Mesoporous silica nanoparticles: a review. *J. Dev. Drugs* 6 (2017).

24. Narayan, R., Nayak, U. Y., Raichur, A. M. & Garg, S. Mesoporous silica nanoparticles: A comprehensive review on synthesis and recent advances. *Pharmaceutics, 10*, 118 (2018).

25. Jeelani, P. G., Mulay, P., Venkat, R. & Ramalingam, C. Multifaceted application of silica nanoparticles. A review. *Silicon, 12*, 1337–1354 (2020).

26. Bahadorikhalili, S., Ma’mani, L., Mahdavi, H. & Shafiee, A. Copper supported β-cyclodextrin functionalized PEGylated mesoporous silica nanoparticle-graphene oxide hybrid: An efficient and recyclable nano-catalyst for straightforward synthesis of 2-arylbenzimidazoles and 1, 2, 3-triazoles. *Microporous and Mesoporous Materials, 262*, 207–216 (2018).

27. Sayahi, M. H., Bahadorikhalili, S., Saghanezhad, S. J., Miller, M. A. & Mahdavi, M. Sulfonic acid-functionalized poly (4-styrenesulfonic acid) mesoporous graphene oxide hybrid for one-pot preparation of coumarin-based pyrido [2, 3-d] pyrimidine-dione derivatives. *Research on Chemical Intermediates, 46*, 491–507 (2020).

28. Bharti, C., Nagaich, U., Pal, A. K. & Gulati, N. Mesoporous silica nanoparticles in target drug delivery system: A review. *International journal of pharmaceutical investigation, 5*, 124 (2015).

29. Moreira, A. F., Dias, D. R. & Correia, I. J. Stimuli-responsive mesoporous silica nanoparticles for cancer therapy: A review. *Microporous and Mesoporous Materials, 236*, 141–157 (2016).
30. Rosenholm, J. M., Zhang, J., Linden, M. & Sahlgren, C. Mesoporous silica nanoparticles in tissue engineering—a perspective. *Nanomedicine, 11*, 391–402 (2016).

31. Zarandi, A. F. Air Pollution Method: A new method based on ionic liquid passed on mesoporous silica nanoparticles for removal of manganese dust in the workplace air. *Analytical Methods in Environmental Chemistry Journal, 2*, 5–14 (2019).

32. Li, D. *et al.* Functionalized magnetic mesoporous silica nanoparticles for U removal from low and high pH groundwater. *Journal of Hazardous Materials, 317*, 494–502 (2016).

33. Gao, J. *et al.* Dopamine functionalized tannic-acid-templated mesoporous silica nanoparticles as a new sorbent for the efficient removal of Cu $^{2+}$ from aqueous solution. *Sci. Rep, 7*, 1–11 (2017).

34. Lee, B., Ma, Z., Zhang, Z., Park, C. & Dai, S. Influences of synthesis conditions and mesoporous structures on the gold nanoparticles supported on mesoporous silica hosts. *Microporous and Mesoporous Materials, 122*, 160–167 (2009).

35. Han, Y. F. *et al.* Controlled synthesis, characterization, and catalytic properties of Mn2O3 and Mn3O4 nanoparticles supported on mesoporous silica SBA-15. *The Journal of Physical Chemistry B, 110*, 24450–24456 (2006).

36. Xu, J., Qu, Z., Wang, Y. & Huang, B. HCHO oxidation over highly dispersed Au nanoparticles supported on mesoporous silica with superior activity and stability. *Catal. Today, 327*, 210–219 (2019).

37. Sarkar, C. *et al.* Interface engineering of graphene-supported Cu nanoparticles encapsulated by mesoporous silica for size-dependent catalytic oxidative coupling of aromatic amines. *ACS applied materials & interfaces, 11*, 11722–11735 (2019).

38. Hu, G. *et al.* Substantially reduced crystallization temperature of SBA-15 mesoporous silica in NaNO3 molten salt. *Mater. Lett, 170*, 179–182 (2016).

39. Chaudhary, V. & Sharma, S. An overview of ordered mesoporous material SBA-15: synthesis, functionalization and application in oxidation reactions. *Journal of Porous Materials, 24*, 741–749 (2017).

**Figures**
Figure 1

(a) TEM; (b) SEM; (c) EDS; and (d) XRD results of Pd@Py2PZ@MSN catalyst.

Figure 2

(a) FT-IR; and (b) TGA results of Pd@Py2PZ@MSN catalyst.
Figure 3

Recovery results of Pd@Py2PZ@MSN catalyst.

Figure 4

SEM image of the recovered Pd@Py2PZ@MSN catalyst.

Supplementary Files
This is a list of supplementary files associated with this preprint. Click to download.

- GraphicalAbstract.tif
- Scheme1.docx