

PdCl₂ Immobilized on Poly(styrene-co-maleimide) as an Effective Heterogeneous Catalyst for Suzuki Cross-Coupling Reaction

S. Soltani^a, N. Montazeri^{a,*}, M. M. Heravi^b, and M. M. Zeydi^a

^a Department of Chemistry, Faculty of Sciences, Islamic Azad University, Tonekabon Branch, Tonekabon, 4684161167 Iran

^b Department of Chemistry, School of Science, Alzahra University, Vanak, Tehran, 1993893973 Iran

*e-mail: n.montazeri20@gmail.com

Received December 3 2019; revised March 16 2020; accepted March 18 2020

Abstract—Poly(styrene-co-maleic anhydride) (SMA) was reacted with 4-amino-6-methyl-3-thioxo-1,2,4-triazine-5-one to obtain the corresponding imide [SMI] which was used as a substrate for immobilization of PdCl₂ and preparation of palladium nanoparticles (PdNPs). The supported PdNPs were fully characterized using scanning electron microscopy (SEM), energy dispersive X-ray (EDAX) and FTIR spectroscopy, and inductively coupled plasma spectrometry (ICP). The catalytic efficiency of the PdNPs was evaluated examined successfully in one the established and useful reaction so-called the Suzuki cross-coupling reaction involving the reaction of various aryl halides with phenylboronic acid in water. The advantages of this procedure include easy recovery and efficient reusability of the expensive PdNPs, high yields of the cross coupled products, short reaction times, and use of water as a green solvent for a wide range of substrates.

Keywords: poly(styrene-co-maleic anhydride) [SMA], polymer support, PdCl₂, Suzuki cross-coupling reaction, boronic acid, SMI–PdCl₂

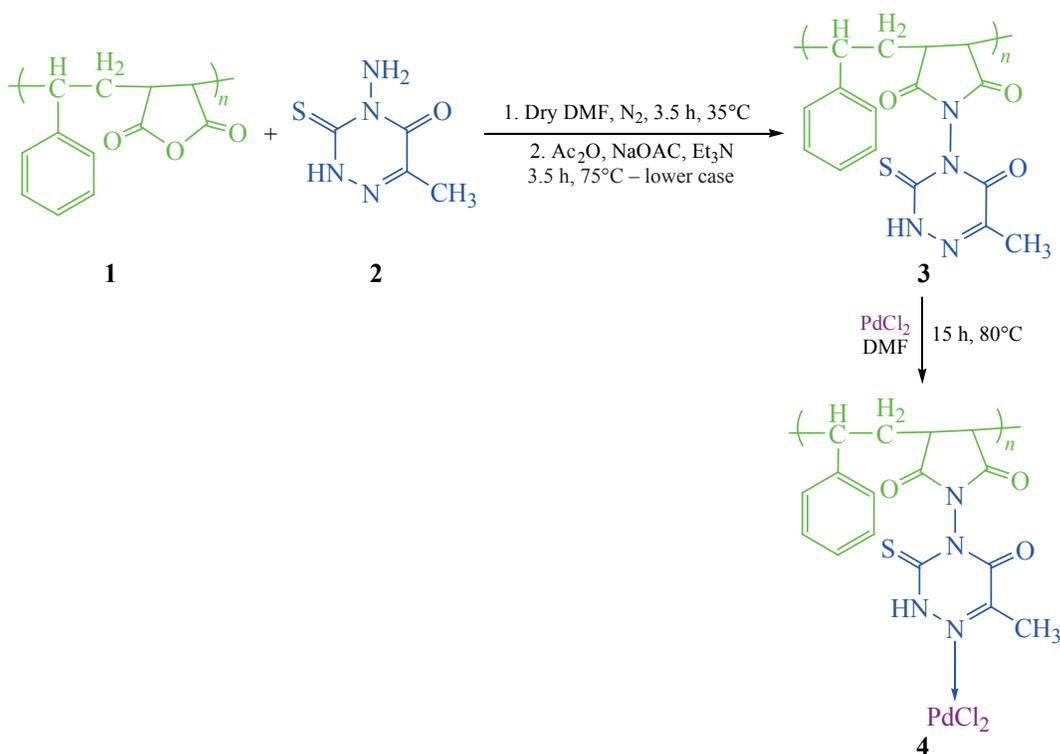
DOI: 10.1134/S1070428020050231

The Suzuki cross-coupling reaction is widely used in the synthesis of natural products [1–3]. Recently, this reaction has drawn special attention due to successful use of intramolecular Suzuki cross-coupling for cyclizations and heterocyclizations [4]. Introduction of new catalysts to promote the cross coupling reactions is considered a significant objective in organic chemistry. Many efforts have been focused on the development of nanocatalysts due to the high and unique activities in the field of catalytic organic transformations [5]. Along with the high efficiency, the advantages of nanocatalysts include cost-effectiveness, low chemical waste, low heat and energy consumption, high safety, and optimal use of starting chemicals [6]. Metal nanoparticles, in particular, palladium nanoparticles (PdNPs), are among the most useful catalysts for both organic and inorganic transformations. The immobilization of PdNPs on different mesoporous and polymeric supports provides heterogeneous catalysts with a well-established capability for easy separation and reusability without considerable loss in catalytic activity [7]. Applications

of PdNPs catalysts have always been one of the most fascinating research fields in green chemistry [8]. The most important Pd-catalyzed reactions include Suzuki [9], Sonogashira [10], Heck [11], Kumada [12] and Stille reactions [13]. Although, Pd catalysts are very useful in academia and industry, their utilization suffers from some disadvantages. They are rather expensive and cannot be easily separated from the reaction mixture. In these cases, using immobilized PdNPs on an appropriate support decreases their drawbacks, making them desirable as a catalyst from the economical point of view. In recent decades, poly(styrene-co-maleic anhydride) [SMA] is known as a commercially available and sensitive co-polymer which can be modified using various nucleophilic agents. Moreover, it is used as an attractive support for designing different reagents and catalysts [14]. The SMA polymer can be modified to an *N*-substituted maleimide [SMI] [15].

Proceeding with our studies regarding organic reactions and preparation of catalysts [16], in the present

Scheme 1.



work we synthesized a modified SMA using a simple coordinating agent, 4-amino-6-methyl-3-thioxo-1,2,4-triazine-5-one, and explored the activity of this newly synthesized substrate for preparing a Pd-supported catalyst. The efficiency, reusability, and recyclability of this catalyst were checked in the Suzuki coupling reaction under green conditions.

The modification of SMA (**1**) with 4-amino-6-methyl-3-thioxo-1,2,4-triazine-5-one (**2**) was successfully performed in two steps following the procedure of Lee et al. [17] (Scheme 1). In the ¹H NMR spectrum of SMI in DMSO, the triazine NH and CH₃ protons appeared as two singlets at 12.09 and 1.92 ppm, respectively. The aromatic proton signals were observed in the range 6.61–7.92 ppm and the aliphatic proton signals, in the range 0.70–2.28 ppm. Such ¹H NMR spectrum confirms the proposed polymer structure (Fig. 1).

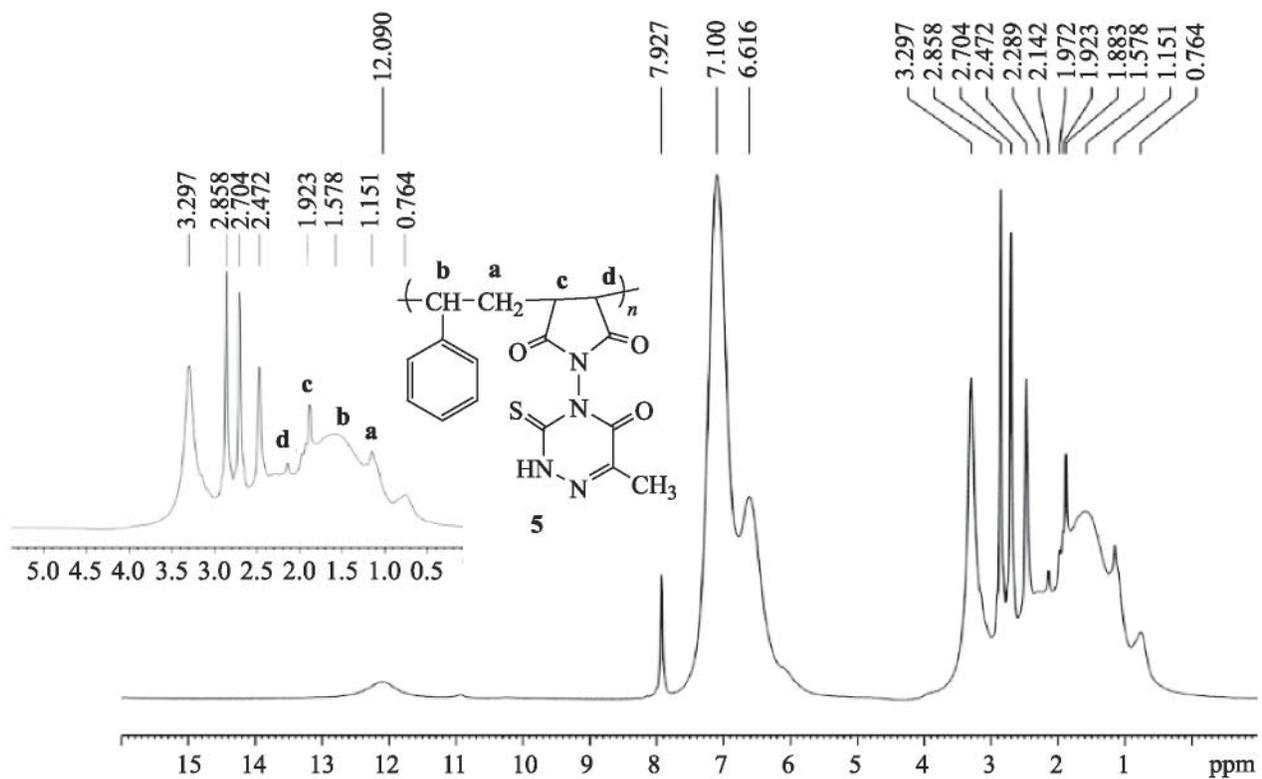
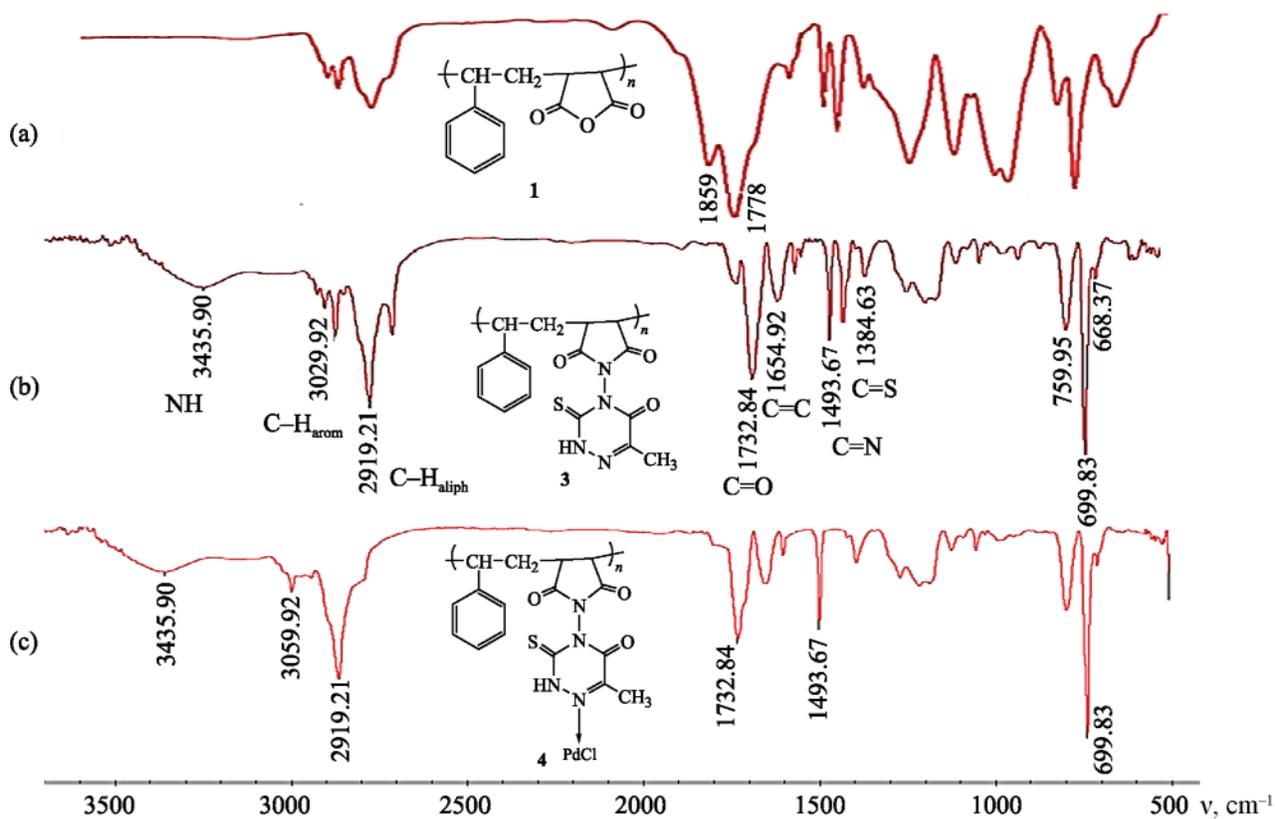
Furthermore, the conversion of the maleic anhydride moiety in SMA to maleimide in SMI was monitored by FTIR spectroscopy. Figure 2 shows that, after the reaction of SMA with 4-amino-6-methyl-3-thioxo-1,2,4-triazine-5-one, a new imide band appeared at 1732 cm⁻¹, and no NH₂ band was observed at 3500 cm⁻¹.

These observations were considered as evidence for complete imidization of SMA and complete consumption of 4-amino-6-methyl-3-thioxo-1,2,4-triazine-5-one. The bands in the range 1300–1700 cm⁻¹ were attributed to the ν(C=C), ν(C=N), and ν(C=S) vibrations of the aromatic rings.

In the FTIR spectrum of the polymer-supported palladium complex, the ν(C=C), ν(C=N), and ν(C=S) bands were slightly shifted to the longwave region, implying chelation of palladium to the triazine nitrogen atom. Therefore, the polymer support can act as a multidentate chelate, increasing the amount of palladium in the catalyst. Indeed, according to the ICP–AES analysis, the concentration of palladium in SMI–PdCl₂ is high (17.34 wt %).

The scanning electron micrographs (Fig. 3) of the supported Pd catalyst clearly showed the morphological changes in the SMI surface produced by the loading with palladium (different size of formations and surface roughness).

The EDAX spectrum of the Pd catalyst (Fig. 4) displayed strong signals of Cl and Pd and weaker signals of N, C, and O atoms, thereby providing evidence to

Fig. 1. ^1H NMR spectrum of SMI.Fig. 2. FTIR spectra of (a) SMA, (b) SMI, and (c) SMI-PdCl₂.

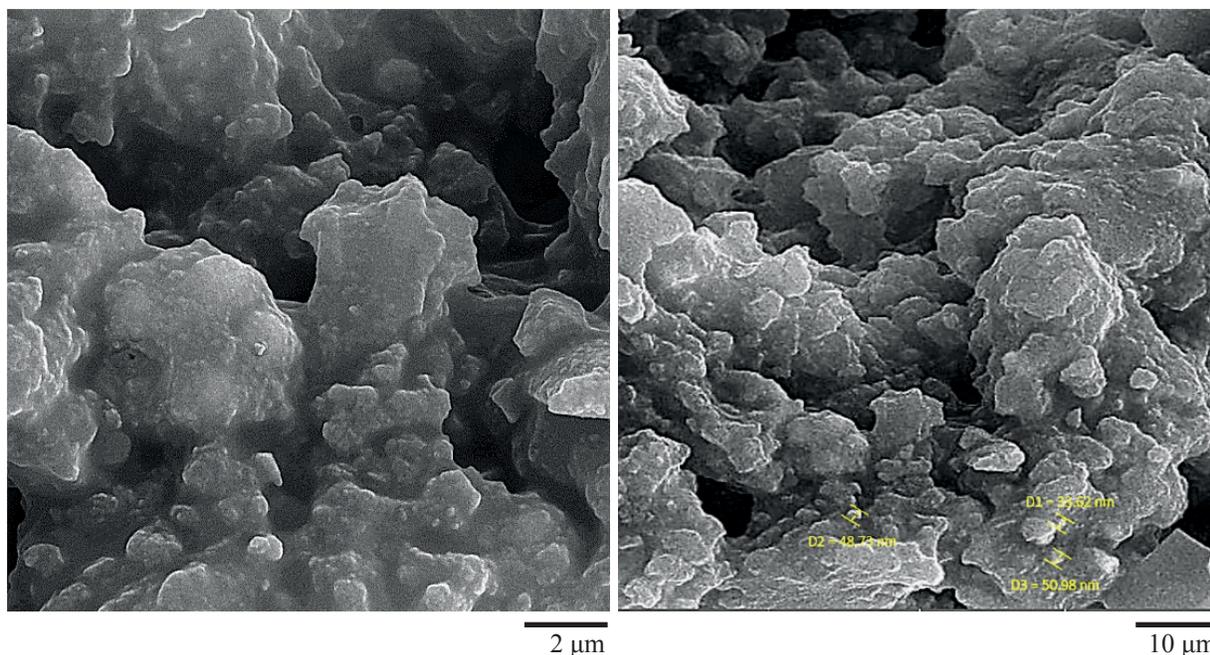


Fig. 3. SEM image of SMI-PdCl₂.

show the nano catalyst was composed of Pd and SMI (Fig. 4).

To test the potency of Pd-supported catalyst, we made use of the Suzuki coupling reaction between phenylboronic acid (**5**) and various aryl halides **6**. The effects of base, solvent, and reaction temperature were screened to optimize the reaction conditions for the coupling of iodobenzene (1.0 mmol) with phenylboronic acid (1.5 mmol) to form biphenyls **7** as the model reaction (Scheme 2, Table 1).

In the Suzuki coupling reaction, the solvent plays a crucial role in the rate and product distribution. As shown by Bedford et al. [18], water profoundly increases the activity of Suzuki–Miyaura catalysts. Therefore, we used H₂O and MeOH–H₂O (3 : 1, v/v) as green and conditionally green solvents, respectively. Even though the experimental results showed that the reaction time in MeOH–H₂O (3 : 1 v/v) was shorter, (Table 1, entry 1), we chose straight H₂O (Table 1, entries 2, 6–15) as an inexpensive, green, readily available, non-inflammable, and non-toxic solvent [19]. In addition, using water as the solvent not only minimizes homocoupling of phenylboronic acid, but also allows easy separation of the desired product from the homo coupled product, due to the different water solubility of these two products [18]. Furthermore, the best results were obtained with 0.02 g of the catalyst under reflux

(Table 1, entries 6–8). As expected, in the absence of any base, virtually no reaction took place (Table 1, entry 9). For selecting appropriate base, such bases as K₂CO₃, Na₃PO₄, NaOAc, NaOH, pyridine, and NEt₃ were tested. As a result, we found that inorganic bases were more effective than organic bases. K₂CO₃, as an easily available and inexpensive chemical, was selected as an optimal base (Table 1, entries 10–14). To discriminate the effect of the polymer supported catalyst SMI–PdCl₂, the reaction was performed with PdCl₂ under the same reaction conditions. In this case,

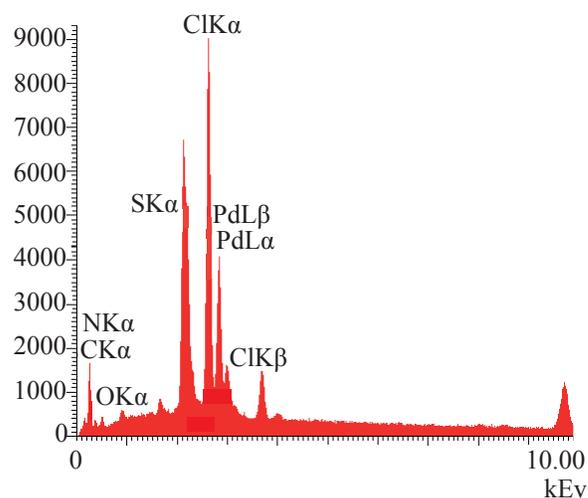
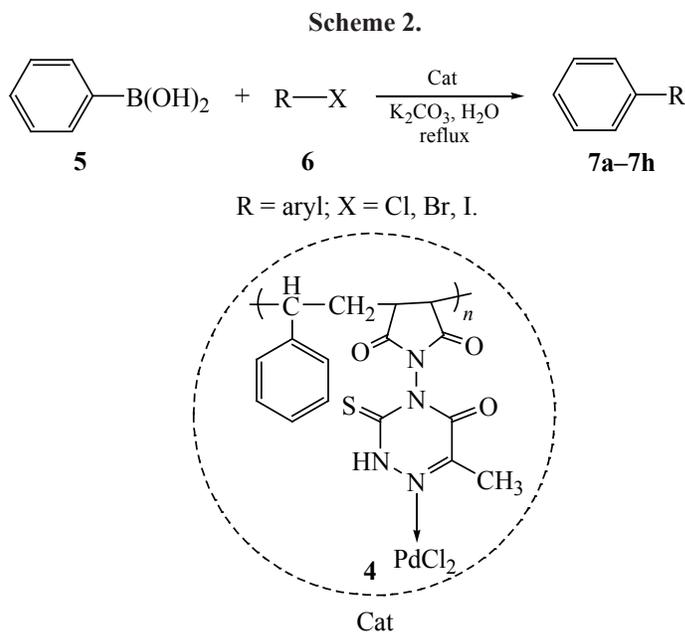


Fig. 4. EDAX spectrum of SMI-PdCl₂.



a significantly lower activity was observed (Table 1, entry 15). Therefore, the Suzuki cross-coupling reaction of various aryl halides (1.0 mmol) and phenylboronic acid (1.5 mmol) were performed in the presence of K_2CO_3 (5 mmol), using 0.02 g of the SMI-PdCl₂ catalyst

(Pd-aryl halide molar ratio 0.018) in water under reflux (Table 2).

We analyzed the electronic and steric effects of electron-donor and electron-acceptor substituents in aryl halides, focusing on the yields and the time required

Table 1. Screening Suzuki reaction conditions of iodobenzene with phenylboronic acid^a

Entry	Solvent	Temperature, C	Base	Catalyst, g	Time, h	Yield, % ^b
1	MeOH/H ₂ O (3 : 1 v/v)	rt	K ₂ CO ₃	0.02	3	95
2	H ₂ O	rt	K ₂ CO ₃	0.02	4	90
3	CH ₃ OH	rt	K ₂ CO ₃	0.02	4	84
4	CH ₃ CN	rt	K ₂ CO ₃	0.02	5	84
5	1,4-Dioxane	rt	K ₂ CO ₃	0.02	5	45
6	H ₂ O	50	K ₂ CO ₃	0.02	3	93
7	H ₂ O	Reflux	K ₂ CO ₃	0.02	2	93
8	H ₂ O	Reflux	K ₂ CO ₃	0.01	4	93
9	H ₂ O	Reflux	–	0.02	2	–
10	H ₂ O	Reflux	Na ₃ PO ₄	0.02	5	62
11	H ₂ O	Reflux	NaOAc	0.02	5	53
12	H ₂ O	Reflux	NaOH	0.02	5	49
13	H ₂ O	Reflux	Pyridine	0.02	5	40
14	H ₂ O	Reflux	NEt ₃	0.02	5	36

^a Iodobenzene (1.0 mmol), phenylboronic acid (1.5 mmol), and base (5.0 mmol).

^b Isolated yield.

Table 2. Suzuki reaction of various aryl halides with phenylboronic acid^a

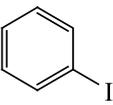
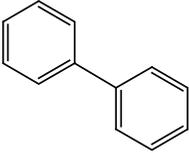
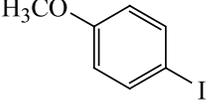
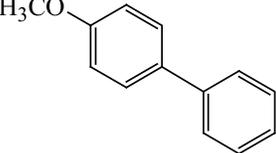
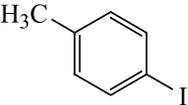
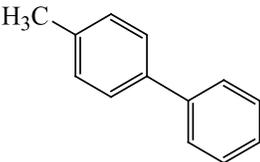
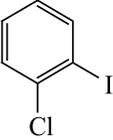
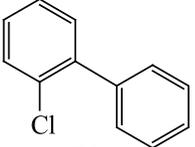
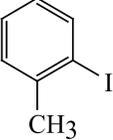
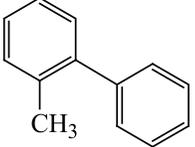
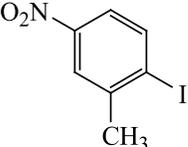
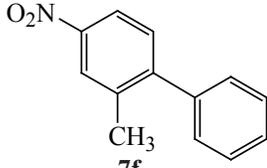
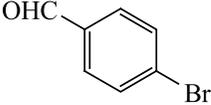
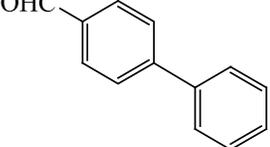
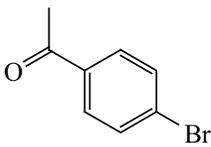
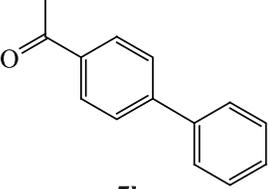
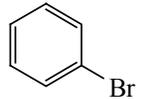
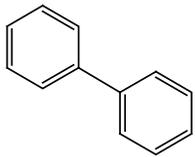
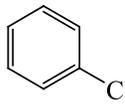
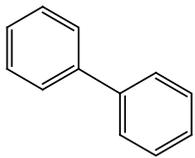
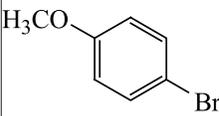
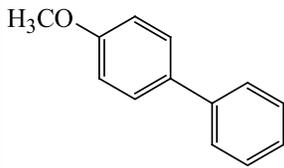
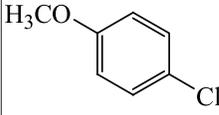
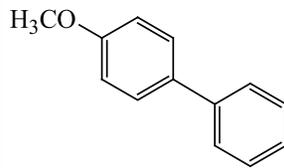
Entry	Substrate	Product	Yield, % ^b	Time, h	TOF, h ^{-1c}	mp, °C (lit. [23])
1		 7a	97	2	26.94	69–71 (70–72)
2		 7b	92	3	17.04	90–92 (91–92)
3		 7c	90	3	16.67	49–53 (45–50)
4		 7d	90	3	16.67	30–34 (32.5–33.5)
5		 7e	72	7	5.71	Colorless oil (colorless oil)
6		 7f	65	8	4.72	52–55 (55–56)
7		 7g	93	2	25.83	54–56 (57–59)
8		 7h	92	2	25.55	117–120 (120–122)

Table 2. (Contd.)

Entry	Substrate	Product	Yield, % ^b	Time, h	TOF, h ^{-1c}	mp, °C (lit. [47])
9		 7a	95	3	17.59	71–74 (70–72)
10		 7a	90	4	12.49	73–75 (70–72)
11		 7b	67	5	7.44	91–93 (91–92)
12		 7b	29	8	2.01	90–93 (91–92)

^a Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K₂CO₃ (5.0 mmol), and SMI–PdCl₂ catalyst (0.02 g).

^b Isolated yield.

^c Turn-over frequency.

for conversion. According to the data in Table 2, both aryl iodides and bromides with both electron-donor and electron-acceptor substituents (entries 1–9) afforded excellent yields of coupling products in reasonable times. However, the couplings of 2-iodotoluene and 2-iodo-5-nitrotoluene with phenylboronic acid resulted in moderate yields of 72 and 65%, respectively (entries 5 and 6, respectively), which can be explained by steric reasons. As known, aryl chlorides are less reactive than aryl iodides and bromides in the Suzuki coupling reactions [20]. In our case, too, the yield and reaction time with chlorobenzene (entry 10) are lower than the respective parameters for bromo- and iodobenzenes (entries 9 and 1, respectively). The turnover frequency (TOF), defined as the mol product/mol catalyst per hour, was calculated from the isolated yield of the product, the amount of palladium, and reaction time. In all reactions, the TOF parameter determined SMI–PdCl₂ as a good catalyst for this kind of reaction (Table 2).

In order to demonstrate the suitability of the catalyst, we compared the results obtained in the synthesis of biaryls with SMI–PdCl₂ with the results of the same reaction with some other catalysts (Table 3). The data in the table show that each method has its own advantages, but SMI–PdCl₂ offers some benefits in terms of low reaction temperature, simple separation, as well as use of a green solvent and no use of additional instruments like a microwave oven. Therefore, we consider our system a better choice.

EXPERIMENTAL

Triethylamine (TEA), *N,N*-dimethylformamide (DMF), and the other chemicals were purchased from Fluka, Merck, and Aldrich (except SMA) and used as received. The public formula of SMA (KARABOND SAM), used in this research, is [(C₈H₈)_{0.6}(C₄H₂O₃)_{0.4}]_n with *M_n* (g/mol) 86.666, *M_w* 182.000, and *M_w/M_n* 2.1. Analysis for Pd was performed by inductively coupled plasma optical emission spectrometry (ICP–OES) on

Table 3. Comparison of the efficiency of SMI–PdCl₂ with different catalysts in the synthesis of biaryls

Entry	Catalyst/Solvent/Conditions	Time	Yield, %	References
1	SMI–PdCl ₂ /H ₂ O/rt	4 h	90	This work
2	TBAB/H ₂ O/100°C	3 h	95	[21]
3	TBAI/H ₂ O/100°C	3 h	90	[21]
4	TBATFB/H ₂ O/100°C	3 h	92	[21]
5	CDBAB/H ₂ O/100°C	3 h	90	[21]
6	CTAB/H ₂ O/100°C	3 h	78	[21]
7	Nano-Fe ₃ O ₄ @AOFc/Pd(II)/Ethanol–H ₂ O/55°C	45 min	88	[22]
8	[OCMCS– 2a –PdCl ₂]/Toluene/100°C	12 h	61	[22]
9	[OCMCS– 5a –PdCl]Cl/Toluene/100°C	60 min	41	[22]
10	(CL–Sc–Pd)/MW, solvent-free/50°C	6 min	59	[22]
11	Pd@Cu–BDC/Py–SI/DMF–H ₂ O/80°C	1 h	94	[22]
12	CelFemImiNHC@Pd/Ethanol/rt	50 min	79	[22]
13	Green chitosan/cellulose–Pd(II)/MW, solvent-free/50°C	5 min	56	[22]
14	CS–NNSB–Pd(II)/MW, solvent-free/50°C	5 min	38	[22]
15	OCS–NS–Pd(II)/MW, solvent-free/50°C	4 min	66	[22]
16	ST–Sc–Pd(II)/MW, solvent-free/50°C	4 min	50	[22]
17	Sporopollenin microcapsule–supported Pd(II)/MW, solvent-free/50°C	6 min	74	[22]
18	Chitosan-pyridyl-based Pd(II)/MW, solvent-free/50°C	5 min	69	[22]
19	Chitosan-Ulva supported Pd(II)/MW, solvent-free/50°C	4 min	47	[22]
20	[OCMCS– 8a –PdCl ₂]/MW, solvent-free/50°C	4 min	65	[22]

Varian 730-ES instrument. The SEM images of the catalyst were obtained on a TeScan-Mira III scanning electron microscope. The X-ray diffraction analysis was performed at room temperature on a PANalytical X'Pert PRO MPD X-ray diffractometer. The chemical composition was determined by energy dispersive X-ray (EDX) elemental analysis on a Lecia Cambridge S 360 scanning electron microscope equipped with EDX probe.

Preparation of SMI (3). Poly(styrene-co-maleic anhydride) (**1**), prepared as described in [14], (1.00 g), 4-amino-6-methyl-3-thiouxo-1,2,4-triazine-5-one (**2**) (1.64 g, 16 mmol), and 15 ml of dry DMF were loaded into a 100-mL three-necked flask, and the mixture was stirred for 3.5 h at 35°C (heating on an oil bath) under nitrogen. Sodium acetate (0.33 g), acetic anhydride (sodium acetate, 0.6 mL), and 0.3 mL of triethylamine were then added to the reaction mixture with syringe.

The temperature was raised to 75°C and stirring was continued for an additional 3.5 h. After cooling to room temperature, 300 mL of rotating methanol was slowly added. The precipitated polymer was washed several times with methanol, and dried at 70°C. For further purification polymer **3** was reprecipitated twice. The amine content of the product was measured by back titration with 0.2 N NaOH [19].

FTIR spectrum, ν , cm^{-1} (KBr disc): 3435 [$\nu(\text{N-H})$], 3026–3059 [$\nu(\text{C-H}_{\text{arom}})$], 2849–2919 [$\nu(\text{C-H}_{\text{aliph}})$], 1732–1782 [$\nu(\text{C=O})$], 1453–1654 [$\nu(\text{C=C})$, $\nu(\text{C=N})$], 1384 [$\nu(\text{C=S})$]. ^1H NMR spectrum (250.13 MHz, $\text{DMSO-}d_6$), δ , ppm: 12.09 s (1H, NH), 6.61–7.92 m (34H, CH), 2.28 m (1H, CH), 1.97–2.14 m (1H, CH), 1.92 s (3H, CH_3), 1.57–1.88 m (1H, CH), 0.7–1.15 m (2H, CH_2).

Preparation of SMI-PdCl₂ (4). A mixture of SMI polymer **3** (1.0 g), PdCl₂ (1.0 g, 3 mmol), and 10 mL DMF was heated at 80°C for 15 h. After completion of the reaction, the precipitated brown polymer was filtered off, washed with acetonitrile (2 × 20 mL), and dried under vacuum at 60°C to give SMI-PdCl₂ **4**. To estimate of the palladium extent, SMI-PdCl₂ (30 mg) was reacted with 5 mL of a mixture of hydrochloric and nitric acids (3 : 1, v/v) at 100°C for 4 h. The mixture was then filtered, and the recovered polymer was washed with distilled water (6 × 2.5 mL), poured with 50 mL of distilled water and analyzed by ICP-OES.

General procedure for the Suzuki coupling reaction 7a–7h. A mixture of aryl halide **6** (1.0 mmol), phenylboronic acid **5** (1.5 mmol, 0.18 g), K₂CO₃ (5.0 mmol, 0.69 g), H₂O (5 mL), and 0.02 g of SMI-PdCl₂ was stirred under reflux. Reaction progress was monitored by TLC in hexane–ethyl acetate (2 : 5). After completion of the reaction, the precipitate that formed was filtered off, washed with several portions of acetone, and dried under reduced pressure at 70°C for 3 h. The product was extracted with CH₂Cl₂ (3 × 5 mL), and the solvent was removed on a rotary evaporator. The crude product was purified by flash column chromatography (hexane or hexane–ethyl acetate). Biaryls **7a–7h** were characterized by their melting points and IR and ^1H NMR spectra and comparison of their physical data with the literature [23, 24].

The IR and ^1H NMR data for selected compounds are as follows.

1,1'-Biphenyl (7a). White solid, mp 69–71°C. FTIR spectrum, ν , cm^{-1} (KBr disc): 3033–3058 [$\nu(\text{C-H}_{\text{arom}})$],

1450–1596 [$\nu(\text{C=C})$], 694–729 [$\nu(\text{C-H})$]. ^1H NMR spectrum (400 MHz, CDCl₃), δ , ppm: 7.59 d (4H), 7.39–7.43 m (4H), 7.30–7.33 m (2H).

4-Methoxybiphenyl (7b). White solid, mp 90–92°C. FTIR spectrum, ν , cm^{-1} (KBr disc): 3000–3056 [$\nu(\text{C-H}_{\text{arom}})$], 1444–1604 [$\nu(\text{C=C})$], 687–844 [$\nu(\text{C-H})$]. ^1H NMR spectrum (250 MHz, $\text{DMSO-}d_6$), δ , ppm: 7.55–7.60 m (4H), 7.43–7.47 m (2H), 7.32–7.35 m (1H), 7.00–7.03 m (2H), 3.89 s (3H).

4-Methylbiphenyl (7c). White solid, mp 44–46°C. FTIR spectrum, ν , cm^{-1} (KBr disc): 3050 [$\nu(\text{C-H}_{\text{arom}})$], 1486 [$\nu(\text{C=C})$]. ^1H NMR spectrum (250 MHz, $\text{DMSO-}d_6$), δ , ppm: 7.58 t (2H, J 7.6 Hz), 7.49 d (2H, J 8.0 Hz), 7.39–7.43 m (2H), 7.33 t (1H, J 7.6 Hz), 7.25 t (2H, J 8.0 Hz), 2.38 s (3H).

CONCLUSIONS

To conclude, we synthesized a novel efficient and green polymer-supported palladium catalyst for the Suzuki reaction. The catalyst exhibited not only high activity, but also afforded a wide range of coupling products in good to excellent yields. In addition, the catalyst is stable in the reaction conditions and can be used without preactivation and recycled in at least five consecutive cycles without appreciable loss of activity. These benefits make the synthesized supported palladium catalyst an interesting and promising alternative to other heterogeneous palladium catalytic systems.

ACKNOWLEDGMENTS

The partial support of this research by the Tonekabon Branch, Islamic Azad University, is gratefully acknowledged. MMH also is grateful to the Alzahra University and the Iran National Science Foundation (INSF) for the granted, awarded individual research chair.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

REFERENCES

1. Beletskaya, I.P., Alonso, F., and Tyurin, V., *Coord. Chem. Rev.*, 2019, vol. 385, p. 137. <https://doi.org/10.1016/j.ccr.2019.01.012>
2. Rocard, L., and Hudhomme, P., *Catalysts*, 2019, vol. 9, p. 1. <https://doi.org/10.3390/catal9030213>
3. Hooshmand, S.E., Heidari, B., Sedghi, R., and Varma, R.S., *Green Chem.*, 2019, vol. 21, p. 381. <https://doi.org/10.1039/C8GC02860E>

4. Heravi, M.M. and Hashemi, E., *Monatsh. Chem.*, 2012, vol. 143, p. 861.
<https://doi.org/10.1007/s00706-012-0746-0>
5. Li, Y., Hong, X.M., Collard, D.M., and El-Sayed, M.A., *Am. Chem. Soc.*, 2000, vol. 15, p. 2385.
<https://doi.org/10.1021/ol0061687>
6. Hemalatha, K., Madhumitha, G., Kajbafvala, A., Anupama, N., Sompalle, R., and Roopan, M., *J. Nanomater.*, 2013, vol. 2013, p. 1.
<https://doi.org/10.1155/2013/341015>
7. Sadjadi, S., Malmir, M., Heravi, M.M., and Ghoreyshi, F., *Int. J. Biol. Macromol.*, 2018, vol. 118, p. 1903.
<https://doi.org/10.1016/j.ijbiomac.2018.07.053>
8. Sadjadi, S., Malmir, M., and Heravi, M.M., *Carbohydr. Polym.*, 2018, vol. 186, p. 25.
<https://doi.org/10.1016/j.carbpol.2018.01.023>
9. Koshvandi, A.T.K., Heravi, M.M., and Momeni, T., *Appl. Organomet. Chem.*, 2018, vol. 32 p. 1.
<https://doi.org/10.1002/aoc.4210>
10. Heravi, M.M. and Sadjadi, S., *Tetrahedron*, 2009, vol. 65, p. 7761.
<https://doi.org/10.1016/j.tet.2009.06.028>
11. Heravi, M.M. and Fazeli, A., *Heterocycles*, 2010, vol. 81, p. 1979.
<https://doi.org/10.3987/REV-10-675>
12. Heravi, M.M. and Hajiabbasi, P., *Monatsh. Chem.*, 2012, vol. 143, p. 1575.
<https://doi.org/10.1007/s00706-012-0838-x>
13. Heravi, M.M. and Mohammadkhani, L., *J. Organomet. Chem.*, 2018, vol. 869, p. 106.
<https://doi.org/10.1016/j.jorganchem.2018.05.018>
14. Thomas, J.M., *Angew. Chem. Int. Ed.*, 2009, vol. 48, p. 3390.
<https://doi.org/10.1002/anie.200901598>
15. Pu, H., Liu, L., Jiang, W., Li, X., and Chen, J.J., *J. Appl. Polym. Sci.*, 2008, vol. 108, p. 1378.
<https://doi.org/10.1002/app.27809>
16. Heravi, M.M., Hashemi, E., Shirazi-Beheshtiha, Y., Ahmadi, S., and Hosseinejad, T., *J. Mol. Catal. A Chem.*, 2014, vol. 394, p. 74.
<https://doi.org/10.1016/j.molcata.2014.07.001>
17. Lee, S.S. and Ahn, T.O., *J. Appl. Polym. Sci.*, 1999, vol. 71, p. 1187.
[https://doi.org/10.1002/\(SICI\)1097-4628\(19990214\)71:7<1187::AID-APP17>3.0.CO;2-N](https://doi.org/10.1002/(SICI)1097-4628(19990214)71:7<1187::AID-APP17>3.0.CO;2-N)
18. Bedford, R.B., Cazin, C.S.J., Coles, S.J., Gelbrich, T., Horton, P.N., Hursthouse, M.E., and Light, M.E., *Organometallics*, 2003, vol. 22, p. 987.
<https://doi.org/10.1021/om020841>
19. Heravi, M.M., Hashemi, E., Shirazi Beheshtiha, Y., Ahmadi, S., and Hosseinejad, T., *J. Mol. Catal. A Chem.*, 2014, vol. 394, p. 74.
<https://doi.org/10.1016/j.molcata.2014.07.001>
20. Littke, A.F. and Fu, G.C., *Angew. Chem.*, 2002, vol. 114, p. 4350.
[https://doi.org/10.1002/1521-3757\(20021115\)114:22<4350::AID-ANGE4350>3.0.CO;2-0](https://doi.org/10.1002/1521-3757(20021115)114:22<4350::AID-ANGE4350>3.0.CO;2-0)
21. Khormi, A.Y., Farghaly, T.A., and Shaaban, M.R., *Helvion*, 2019, vol. 5, p. 1.
<https://doi.org/10.1016/j.helivion.2019.e01367>
22. Sabaqian, S., Nemati, F., Taherpour Nahzomi, H., and Heravi, M.M., *Carbohydr. Polym.*, 2017, vol. 177, p. 165.
<https://doi.org/10.1016/j.carbpol.2017.08.109>
23. Xu, Q., Duan, W.L., Lei, Z.Y., Zhu, Z.B., and Shi, M., *Tetrahedron*, 2005, vol. 61, p. 11225.
<https://doi.org/10.1016/j.tet.2005.09.010>
24. Yu, Y., Hu, T., Chen, X., Xu, K., Zhang, J., and Huang, J., *Chem. Commun.*, 2011, vol. 47, p. 3592.
<https://doi.org/10.1039/C0CC04498A>