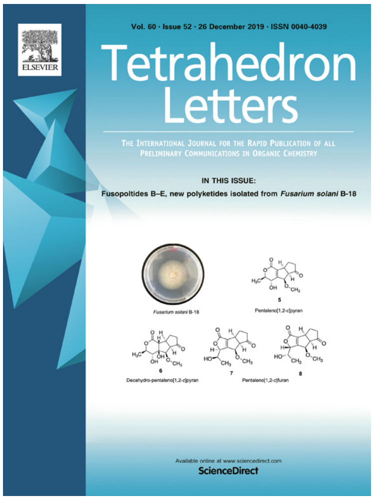
Journal Pre-proofs



Magnetic Nanoparticles-Supported Palladium catalyzed Suzuki-Miyaura Cross Coupling

Sandip P. Vibhute, Pradeep M. Mhaldar, Rajendra V. Shejwal, Dattaprasad M. Pore

PII: S0040-4039(20)30003-4
DOI: https://doi.org/10.1016/j.tetlet.2020.151594
Reference: TETL 151594

To appear in: *Tetrahedron Letters*

Received Date: 5 November 2019
Revised Date: 2 January 2020
Accepted Date: 3 January 2020

Please cite this article as: Vibhute, S.P., Mhaldar, P.M., Shejwal, R.V., Pore, D.M., Magnetic Nanoparticles-Supported Palladium catalyzed Suzuki-Miyaura Cross Coupling, *Tetrahedron Letters* (2020), doi: https://doi.org/10.1016/j.tetlet.2020.151594

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier Ltd.

Journal Pre-proofs

Tetrahedron Letters
journal homepage: www.elsevier.com

Magnetic Nanoparticles-Supported Palladium catalyzed Suzuki-Miyaura Cross Coupling

Sandip P. Vibhute[a,b], Pradeep M. Mhaldar[a], Rajendra V. Shejwal[b], Dattaprasad M. Pore[a*]

[a]*Department of Chemistry, Shivaji University, Kolhapur- 416004, India *E-mail: p_dattaprasad@rediffmail.com*
[b]*Lal Bahadur Shastri College of Arts, Science and Commerce, Satara., India*

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

ABSTRACT

A new magnetic nanoparticles-supported palladium(II) nanomagnetic catalyst (Pd-AcAc-Am-Fe_3O_4@SiO_2) was synthesized and characterized using attenuated total reflectance infrared spectroscopy (ATR-IR), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), energy-dispersive X-ray spectroscopy (EDS), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM). The nanomagnetic catalyst was used as convenient and efficient catalyst for the Suzuki–Miyaura cross-coupling of various aryl bromides/chlorides/iodides with phenylboronic acid. The effects of varying solvents, base, temperature, reaction time and catalyst amount on the performance of the Suzuki– Miyaura cross-coupling reaction were investigated. The notable advantages of this heterogeneous nanomagnetic catalyst are excellent yields, mild reaction conditions, short reaction times and easy magnetic work-up and recyclability. Moreover, the new nanomagnetic catalyst could be easily recovered with an external magnet and could be reused at least six times without significant loss of its catalytic activity.

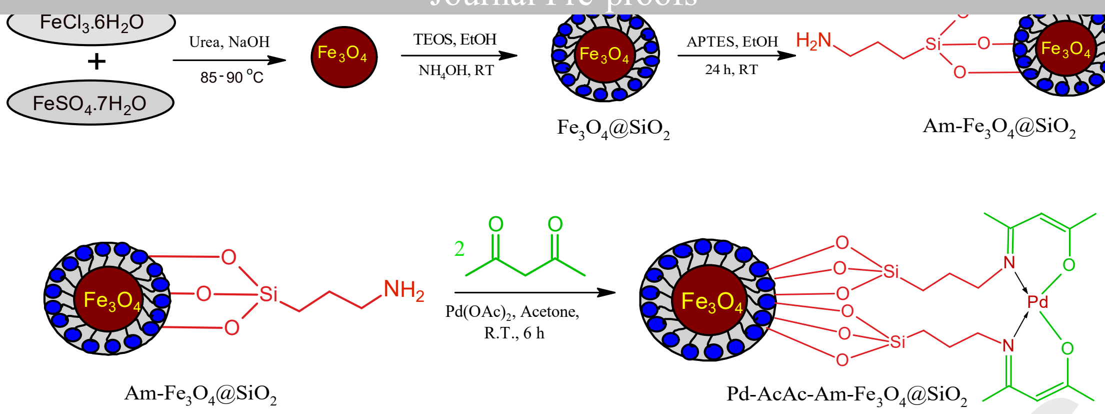
Keywords: Magnetic Nanoparticles , Suzuki-Miyaura, Heterogeneous, Reusability

2009 Elsevier Ltd. All rights reserved.

1. Introduction

The palladium-catalyzed Suzuki–Miyaura cross coupling is one of the most valuable synthetic methods for synthesis of biaryls, which play an important role as a partial structures in pharmaceuticals, natural products, agrochemicals and in the field of engineering materials such as molecular wires, liquid crystals and conducting polymers [1-9]. Till date, numerous homogeneous as well as heterogeneous catalysts have been developed for Suzuki–Miyaura cross-coupling reactions [10–22]. Among these, homogeneous Schiff base–transition metal complexes have been found to exhibit excellent catalytic activities which inspired researchers to develop several homogeneous catalysts equipped with Schiff base–transition metal complexes [23–26]. However, a major drawback of homogeneous catalysts is the difficulty in their separation from the reaction mixture that prohibits recovery and reuse. Current economical factors in the large-scale synthesis and environmental concerns compel the scientific community to develop catalysts that would be recyclable and reusable several times. Hence, huge efforts have been made for the design and development of various heterogeneous catalysts for Suzuki–Miyaura cross-coupling. Numerous examples of immobilization of Schiff base–transition metal complexes on various supports, such as ferrite [27, 28] zeolite [29, 30] polymer [31-33] and clay [34] have been reported. Inorganic matrices show some advantages over organic supports, such as high thermal, chemical and mechanical stability. The increasing demand for eco-friendly chemical processes has stimulated many researchers across the globe to develop heterogeneous catalysts, which can be recovered easily and reused effectively. Recently, palladium immobilized on the surface of silica was used as a heterogeneous catalyst for the Suzuki-Miyaura cross-coupling reaction [35]. In continuation of our recent investigation of the application of magnetically recyclable catalysts in organic transformations,[36] herein we design and synthesize a new nanomagnetic catalyst, a ferrite supported silica coated amine functionalized Schiff base–palladium(II) complex (Pd-AcAc-Am-Fe_3O_4@SiO_2) for Suzuki–Miyaura cross-coupling of various aryl halides with phenylboronic acid. The synthesized nanomagnetic catalyst was characterized by various spectroscopic and microscopic techniques.

Journal Pre-proofs



Scheme 1: Synthetic route towards preparation of catalyst

2. Result and Discussion

2.1 ATR-IR:

The attenuated total reflectance infrared spectroscopy was used to characterize the functionality in Fe_3O_4, $Fe_3O_4@SiO_2$, Am-$Fe_3O_4@SiO_2$, AcAc-Am-$Fe_3O_4@SiO_2$ and Pd (II)-AcAc-Am-$Fe_3O_4@SiO_2$ [Fig. 1]. The presence of stretching vibration band at 555 cm^{-1} with a slight splitting is attributed to Fe-O bond in magnetite (Fe_3O_4) [38]. The silica coating of magnetite nanoparticles was confirmed by observation of a broad band at 1071 cm^{-1} which can be assigned to Si-O stretching vibrations. On moving from Fe_3O_4 to $Fe_3O_4@SiO_2$, a significant reduction of the intensity of the Fe-O stretching and bending vibration bands is observed. The characteristic absorption bands observed at 3362 cm^{-1} and 1554 cm^{-1} is due to stretching and bending vibrations of physically adsorbed water and surface O-H groups. The band at 2927 cm^{-1} corresponds to the C-H stretching in CH_2 group of amino-propyl group in functionalized $Fe_3O_4@SiO_2$. The spectrum of the acetyl acetone grafted over Am-$Fe_3O_4@SiO_2$ exhibited a strong band at 1641 cm^{-1} due to C=N stretching vibration. This confirms the covalent binding of ligand on the surface of Am-$Fe_3O_4@SiO_2$. On metallation, palladium binds to the bidentate complex and prominent C=N stretching frequency was shifted to lower wave number, indicating strong metal–ligand interaction.

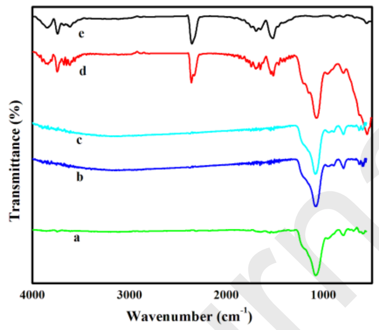


Fig. 1: ATR-IR analysis of a) Fe_3O_4, b) $Fe_3O_4@SiO_2$, c) Am-$Fe_3O_4@SiO_2$, d) AcAc-Am-$Fe_3O_4@SiO_2$, e) Pd-AcAc-Am- $Fe_3O_4@SiO_2$

2.2 TEM and SEM:

For the investigation of particle size, shape and morphology of the synthesized nanocomposites, transmission electron microscopy (TEM) study was conducted. TEM image of final catalyst (Fig. 2a) elucidates the uniform metal binding to the core-shell surface nanocomposites. The TEM image of recovered catalyst (Fig. 2b) has also been provided to confirm that shape and diffraction pattern (Fig. 2c) confirmed the crystallinity of these nanoparticles and was found to be consistent with XRD results.

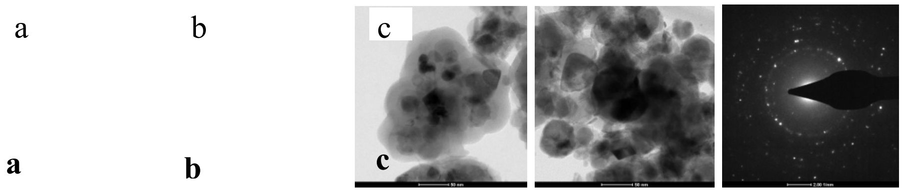


Fig. 2: TEM images of prepared catalyst. Before reaction (a) 50 nm; after sixth run (b) 50 nm (c) SAED.

Another technique that provides considerable amount of information about the topography of the sample is the scanning electron microscopic (SEM) analysis. The transition from smooth surface of MNP to spongy surface confirms the successful coating of MNP by a silica shell (Fig. 3a). The FE-SEM images display spherical morphology of the Pd-AcAc-Am-$Fe_3O_4@SiO_2$ catalyst with slight aggregation and appear same as that of SMNP, thereby suggesting that surface modification processes did not alter the morphology of the nano-catalyst. In addition to this, the SEM image of the recovered catalyst indicates that the shape and morphology of the catalyst remain unaltered (Fig. 3b).

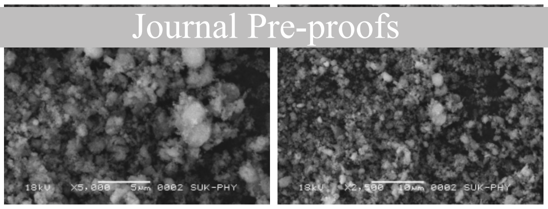


Fig. 3: SEM images of catalyst a) Before reaction b) After reaction

2.3 Elemental and compositional analysis:-

Energy dispersive X-ray spectroscopy (EDX) is a powerful tool for accomplishing the elemental analysis of various samples. The EDX spectrum of Pd-AcAc-Am-Fe_3O_4@SiO_2 (Fig. 4) shows the presence of iron, silicon and oxygen atoms which reveal the existence of a silane shell around the magnetic core material. Apart from these elements, the peaks of nitrogen, carbon and palladium authenticate the successive surface functionalization, ligand immobilization and metallation of the silica encapsulated magnetite nanoparticles, thus by confirming the structure of the final nanocatalyst. The amount of Pd also measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) which was found to be 0.99 wt. %.

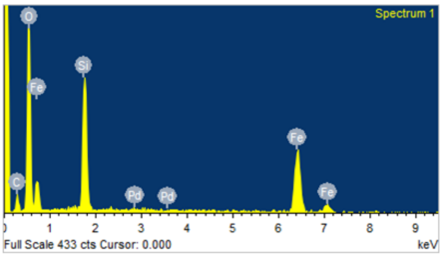


Fig. 4: EDX spectrum of catalyst

2.4 Vibrating Sample Magnetometer:

The magnetic properties of Pd-AcAc-Am-Fe_3O_4@SiO_2 were assessed using a vibrating sample magnetometer (VSM) (Fig.5). The curves exhibit an extremely interesting phenomenon showing a decrease in the values of the saturation magnetization (Ms) of Pd-AcAc-Am-Fe_3O_4@SiO_2 is 34.00 emu/g in comparison with the bulk magnetite nanomaterials that typically show a saturation magnetization value of 92 emu/g. It could be reasoned that the silica coating and the immobilization of various species onto the magnetic nanosupport cause a reduction in the surface moments of the individual particles, eventually resulting in a decrease in the net magnetism possessed by these materials [39]. It is believed that however, despite the lowering of the Ms values, the application of the surface modified nanocomposites remains unaffected as they show a fast response to an applied magnetic field by getting quickly attracted to an external magnet, suggesting that the synthesized nanocatalyst possesses good magnetism and redispersibility.

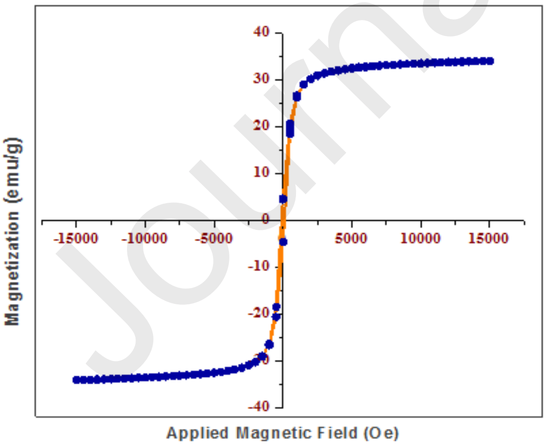


Fig. 5: VSM spectrum of catalyst

2.5 Catalytic Activity of Pd-AcAc-Am- Fe_3O_4@SiO_2 in Suzuki–Miyaura Cross-Coupling Reactions:

After full characterization of the synthesized Pd-AcAc-Am-Fe_3O_4@SiO_2 nanomagnetic catalyst with spectroscopic and microscopic methods, its catalytic potential was investigated as a magnetically separable nanomagnetic catalyst in Suzuki–Miyaura cross coupling reactions. The Suzuki–Miyaura cross-coupling reaction is one of the most important method for C-C bond formation in organic transformations. The Suzuki–Miyaura cross coupling reaction is used in various organic reactions and therefore it now belongs to an essential set of palladium catalyzed cross coupling reactions. Thus, the catalytic potential of the synthesized nanomagnetic catalyst was explored in Suzuki–Miyaura cross coupling reactions. The reaction conditions such as solvent, base, temperature, amount of catalyst loading were optimized for a model Suzuki–Miyaura cross coupling reaction of iodobenzene with phenylboronic acid. Considering the key role of base in the formation of active palladium intermediates and promoting transmetallation during the catalytic cycle of Suzuki–Miyaura cross– coupling reaction, [40] different bases including sodium/potassium inorganic salts and organic base were screened (Table 1, Entries 1–11). It was found that, K_2CO_3 was superior and giving an excellent yield (Table 1, Entry 6). Likewise, we did an experiment in the absence of base, no cross–coupling product was observed, which confirmed the necessity of base for the smooth Suzuki–Miyaura cross–coupling reaction (Table 1, Entry 8).

Journal Pre-proofs

Journal Pre-proofs

Screening of solvents was carried out employing K_2CO_3 as a base with toluene, dioxane, ethanol, THF, Acetonitrile, DMF and DMF:Water mixed solvent system. We observed that yield of the desired product is increased to 98 % in DMF:Water system (8:2, v/v) (Table 2, entry 10). Presence of water in a reaction media increases solubility of the bases, which is responsible for the activation of boronic acid resulting in enhancing the rate of the reaction in aqueous medium [41]. It is noteworthy that, the reaction only in water did not proceed at all probably due to scanty solubility of the reactants in the water (Table 2, Entry 2).

Table 1. Optimization of base and amount of catalyst for Suzuki coupling reaction

Entry	Catalyst (mg)	Base	Yield (%)[a]
1	30	NaOH	75
2	30	KOH	78
3	30	NaOAc	59
4	30	$N(C_2H_5)_3$	52
5	30	K_3PO_4	85
6	**30**	**K_2CO_3**	**98**
7	30	Na_2CO_3	88
8	30	--	No reaction
9	40	K_2CO_3	98
10	20	K_2CO_3	89
11	15	K_2CO_3	84

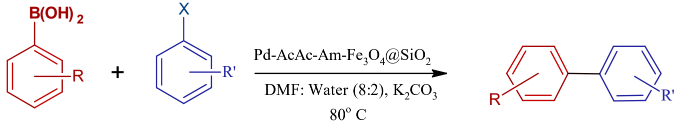
*Reaction conditions: Iodobenzene (1mmol), phenylboronic acid (1.2 mmol), base (3 mmol), catalyst (Pd-acac-am-Fe_3O_4@SiO_2) (0.030 g, 0.28 mol% Pd), temp.= 80 °C, 2 h; solvent = DMF: Water (8:2) 5 mL, [a] Isolated yield

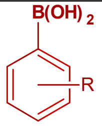
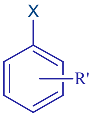
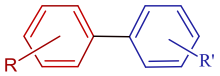
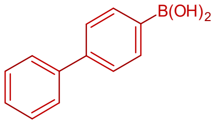
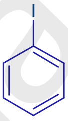
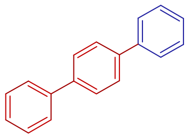
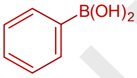
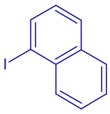
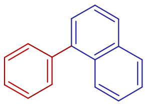
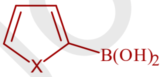
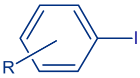
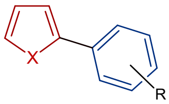
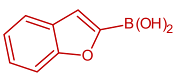
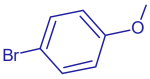
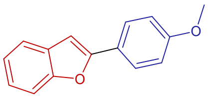
After attaining the optimal reaction conditions, we then examined the applicability of the present catalytic system to the Suzuki–Miyaura cross–coupling of various aryl halides and different aryl boronic acids (Table 3). A wide range of electronically and structurally diverse aryl iodides, bromides and chlorides were readily coupled with different substituted aryl boronic acids in excellent yields. It was observed that, the reaction of aryl halides with electon deficient aryl boronic acid took slightly longer time compared to those of the electron–neutral and electron–rich boronic acids (Table 3, Entries 6-8). Various aryl halides bearing electron–withdrawing groups such as nitro, cyano, aldehyde, acetyl moieties, and electron donating groups such as methyl and methoxy moieties react with different substituted aryl boronic acids to afford biaryls in excellent yields (Table 3, Entries 1–11). It is noteworthy that less activated aryl chlorides bearing either electron-donating or electron-withdrawing substituent afforded corresponding products in excellent yields (Table 3, Entries 12-13).

Further to extend the scope of the catalytic system, we next employed boronic acids possessing heterocyclic moiety as coupling partners for Suzuki–Miyaura cross coupling. Due to the low reactivity of substituted heterocycle [42-44] moderate yield of the target product was obtained (Table 3, Entries 16-18).

Journal Pre-proofs

Table 3. Combinatorial library of biaryls synthesised by Suzuki–Miyaura coupling



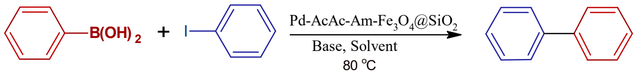
Entry	Aryl boronic acid	Aryl halide	Product	Time (h)	Yield[b] (%)	TON	TOF (h^{-1})
							
1	R = H	R’= 4-H, X= I	R’= 4-H, R= H	1	96	342	342
2	R = H	R’= 4-OCH_3, X= I	R = H; R’= 4-OCH_3	1	96	342	342
3	R = OCH_3	R’= 4-OCH_3, X= I	R = OCH_3; R’= 4-OCH_3	1	96	342	342
4	R = H	R’= 4-CN, X= I	R = H; R’= 4-CN	1	98	350	350
5	R =3-CH_3	R’= 4-CN, X= I	R =3CH_3; R’= 4-CN	1	96	342	342
6	R = H	R’= 4-NO_2, X= I	R = H; R’= 4-NO_2	2	96	342	171
7	R = H	R’= 4-$COCH_3$, X= I	R = H; R’= 4-$COCH_3$	3	80	285	95
8	R = H	R’= 4-CHO, X= I	R = H; R’= 4-CHO	3	92	328	109
9	R = NH_2	R’= 4-Cl, X= I	R = NH_2; R’= 4-Cl	1	95	339	339
10	R = H	R’= 4-CH_3, X= I	R = H; R’= 4-CH_3	1	94	335	335
11	R = H	R’= 4-OCH_3, X= Br	R = H; R’= 4-OCH_3	2	90	321	160
12	R = H	R’= 4-H, X= Cl	R’= 4-H, R= H	1	90	321	321
13	R = NH_2	R’= 4-H, X= Cl	R = NH_2; R’= 4-H	3	86	307	102
14				1	80	286	286
15				1	96	342	342
							
16	X= -S	R= 4-H, X= -I	R= 4-H, X= S	2	89	318	159
17	X= O	R= 4-H, X= -I	R= 4-H, X= O	2	90	321	160
18				2	89	318	159

[a]Reaction conditions: aryl halide (1mmol), phenylboronic acid (1.2 mmol), Pd-acac-Am-$Fe_3O_4@SiO_2$ (0.030 g, 0.28 mol% Pd), K_2CO_3 (3 mmol), DMF:water (8:2), 5 mL, temp = 80 °C; [b]Isolated yield.

Journal Pre-proofs

Journal Pre-proofs

Table 2. Optimization of Solvent for Suzuki cross coupling*



Entry	**Solvent**	**Yield (%)**[a]
1	Ethanol	50
2	Water	NR
3	Acetonitrile	55
4	THF	60
5	Dioxane	68
6	Toulene	72
7	DMF	88
8	DMF: Water (5:5)	82
9	DMF: Water (7:3)	91
10	**DMF: Water (8:2)**	**98**

*Reaction conditions: Iodobenzene (1mmol), phenylboronic acid (1.2 mmol), base K_2CO_3 (3 mmol), catalyst (Pd-acac-am-$Fe_3O_4@SiO_2$) (0.030g, 0.28 mol% Pd), temp.= 80 °C, 2 h; solvent = 5 mL, NR= No Reaction [a] Isolated yield

The comparative study of catalytic activity of Pd-AcAc-Am-$Fe_3O_4@SiO_2$ with the various supported heterogeneous palladium catalysts is depicted in Table 4. It is primarily observed that many of the supported catalysts exhibit the catalytic activity at higher temperature (90 to 110 °C) as compared to Pd-AcAc-Am-$Fe_3O_4@SiO_2$ furnishing lower yields (Table 4, entries 2-4). In addition, some of the catalysts viz Pd@Fe_3O_4, $Fe_3O_4@SiO_2$-Pd and Pd@SMP revealed high yields at ambient temperature but require far longer reaction time (12 h) as compared to present protocol (Table 4, entries 5-7). Moreover, Pd-AcAc-Am-$Fe_3O_4@SiO_2$ is more proficient compared to the MSN-IPr and FeS@EP–AG–Pd with respect to reaction time (Table 4, entries 8-9). Therefore, Pd-AcAc-Am-$Fe_3O_4@SiO_2$ is found to be superior as compared to other reported catalysts producing high yields (87–98%) in short reaction time. It is noteworthy to mention that, unlike in other reported protocols, the catalyst could easily be recovered by applying an external magnet thereby avoiding loss of catalyst during attrition.

Table 4: Comparison of catalytic efficiency of Pd-AcAc-Am-$Fe_3O_4@SiO_2$ with reported catalysts for Suzuki-Miyaura coupling

Sr. No.	Catalyst	Temp °C	Solvent	Time (h)	Yield %	**Ref.**
1	Pd-AcAc-Am-$Fe_3O_4@SiO_2$	80	DMF:H_2O	1	96	This work
2	Maghemite–Pd	110	DMF:H_2O	1	90	45
3	MNP-di(2pyridyl)methanol–Pd	100	DMF	5	92	46
4	Graphene-$Fe_3O_4@SiO_2$@Pd	90	----	0.5	90	47
5	$Fe_3O_4@SiO_2$-Pd	RT	EtOH	12	90	48
6	Pd@Fe_3O_4	45-60	MeOH	12	91	49
7	Pd@SMP	80	Dioxane	15	96	50
8	MSN-IPr	80	^{i}PrOH	2	90	51
9	FeS@EP–AG–Pd	50	Water	2	99	52
10	SBA15/AO/Pd(0)	50	H_2O:EtOH	1	98	53

One of the most important factors in heterogeneous catalysis is catalyst recovery and recycling. The newly synthesized Pd-AcAc-Am-$Fe_3O_4@SiO_2$ nanomagnetic catalyst was successfully recovered by applying an external magnetic field washed thoroughly with ethanol and distilled water and dried at 50 °C for 6 h and reused for next run. It was observed that there was no change in catalytic activity up to 6 recycles without any noticeable loss in yield (Fig. 6). Recycled nanomagnetic catalyst was characterized using SEM and TEM analysis. No significant change in morphology as well as particle size of the nanocatalyst was found.

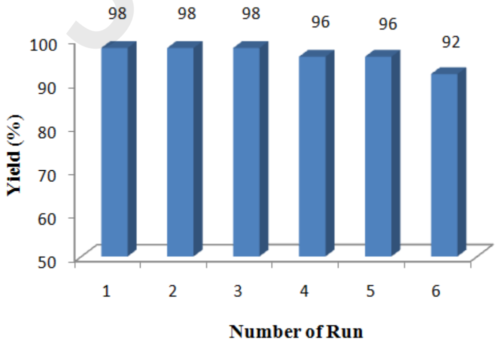


Fig. 6: Reusability of catalyst

Con

Journal Pre-proofs

A new reusable Pd-AcAc-Am-Fe_3O_4@SiO_2 nanomagnetic catalyst was successfully prepared and characterized using ATR-IR, TEM, FE-SEM, EDX, ICP-AES and VSM. The main advantages of the catalyst are simplicity, selectivity, eco-friendliness and ease of recovery using an external magnetic field. The recovered catalyst can be reused up to six cycles without significant loss of catalytic activity. The developed protocol offers many advantages such as broad substrate scope, functional group tolerance, short reaction times, excellent yields, catalyst reusability, etc. making it compatible for industrial scale application.

Acknowledgement:

One of the authors DMP grateful to acknowledge, Shivaji University, Kolhapur for Financial Assist through Research Strengthening Scheme. [SU/C&U.D.Section/89/1386].

References and notes

1. Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, 107, 133-173.
2. Phan, N. T. S.; Van, M.; Der Sluys, C. W. J. *Adv. Synth. Catal.* **2006**, 348, 609-679.
3. Corbet, J.-P.; Mignani, G.; *Chem. Rev.* **2006**, 106, 2651-2710.
4. Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, 102, 1359-1470.
5. Belardi, J. K.; Micalizio, G. C. *Angew. Chem. Int. Ed.* **2008**, 47, 4005-4008.
6. Jia, Y.; Bois-Choussy, M.; Zhu, J. *Angew. Chem. Int. Ed.* **2008,** 47, 4167-4172.
7. Burlison, J. A.; Neckers, L.; Smith, A. B.; Maxwell, A.; Blagg, B. S. J. *J. Am. Chem. Soc.* **2006**, 128, 15529-15536.
8. Nicolaou, K. C.; Li, H.; Boddy, C. N. C.; Ramanjulu, J. M.; Yue, T.-Y.; Natarajan, S.; Chu, X.-J; Bräse, S.; Rübsam, F. *Chem. Eur. J.* **1999**, 5, 2584-2601.
9. Stanforth, S. P. *Tetrahedron* **1998**, 54, 263-303.
10. Veisi, H.; Naja, S.; Hemmati, S. *Int. J. Biol. Macromol*., **2018**, 113, 186–194.
11. Veisi, H.; Gholami, J.; Ueda, H.; Mohammadi, P.; Noroozi, M. *J. Mol. Catal. A: Chem*., **2015**, 396, 216-223.
12. Sydnes, M. O. *Catalysts*, **2017**, 7, 35 -49.
13. Stevens, P. D.; Fan, J.; Gardimalla, H. M. R.; Yen, M.; Gao, Y.; *Org. Lett.* **2005**, 7, 2085 – 2088.
14. Zhang, X.; Li, P.; Ji, Y.; Zhang, L.; Wang, L. *Synthesis* **2011**, 18, 2975–2983.
15. Anuradha, Kumari, S.; Layeka S.; Pathak, D. *New J. Chem*., *2017*, 41, 5595-5604.
16. Yuan, D.; Chen, L.; Yuan, L.; Liao, S.; Yang, M.; Zhang, Q. *Chem Eng J* **2016**, 287, 241–251.
17. Sobhani, S.; Mesbah Falatooni, Z.; Asadi, S.; Honarmand, M. *Catal. Lett.,* **2016**, 146, 255-268.
18. Vishal, K.; Fahlman, B. D.; Sasidhar, B. S.; Patil Shivaputra, A.; Patil Siddappa, A.; *Catal Lett* **2017**,147, 900-918.
19. Jadhav, S. N.; Kumbhar, A. S.; Rode, C. V.; Salunkhe, R. S.; *Green Chem.* **2016**, 18, 1898-1911.
20. Wang, Y.; Liu, Y.; Zhang, W. Q.; Sun, H.; Zhang, K.; Jian, Y.; Gu, Q.; Zhang, G.; Li, J.; Gao, Z. *ChemSusChem* **2019**, 12, 5265-5273.
21. Takale B. S.; Thakore, R. R.; Handa, S.; Gallou, F.; Reilly, J.; Lipshutz, B. H. *Chem. Sci.* **2019**, 10, 8825-8831.
22. Thakore, R. R.; Takale, B. S.; Gallou, F.; Reilly, J.; Lipshutz, B. H. *ACS Catal*. 2019, 9, 11647-11657
23. Dewan, A.; Bora, U.; Borah, G. *Tetrahedron Lett.* **2014**, 55, 1689-1692.
24. Shahnaz, N.; Banik, B.; Das, P. *Tetrahedron Lett.* **2013,** 54, 2886-2889.
25. Patil, S. A.; Weng, C. M.; Huang, P. C.; Hong, F. E. *Tetrahedron* **2009**, 65, 2889-2897.
26. Lai, Y. C.; Chen, H. Y.; Hung, W. C.; Lin, C. C.; Hong, F. E. *Tetrahedron* **2005**, 61, 9484-9489.
27. Gawande, M. B.; Manoj, B.; Monga, Y.; Zboril, R.; Sharma, R.K. *Coord. Chem. Rev*. **2015**, 288, 118-143.
28. Sharma, R. K.; Dutta, S.; Sharma, S.; Zboril, R.; Varma R. S.; Gawande, M. B. *Green Chem*., **2016**, 18, 3184-3209.
29. Rivallan, F. Thomas, M. Lepage, S. Takagi, M. Hirata, N. Thibault-Starzyk, H. *Chem. Cat. Chem.* **2010**, 2, 1599-1605.
30. Bansal, V. K., Thankachan, P. P., Prasad, R. *Appl. Catal. A* **2010**, 381, 8-17.
31. Chang, Y.; Lv, Y.; Lu, F.; Zha, F.; Lei, Z. *J. Mol. Catal. A* **2010**, 320, 56-61.
32. Chang, Y.; Shi, X. L.; Zhu, D. M.; Liu, Y. *Polym. Adv. Technol.* **2008**, 19, 877-881.
33. Sharma, S.; Sinha, S.; Chand, S. *Ind. Eng. Chem. Res*. **2012**, 51, 8806-8814.
34. Li, Z. Y.; Tang, R. R.; Liu, G. Y. *Catal. Lett.* **2013**, 143, 592-599.
35. Baleizão, C.; Corma, A.; García, H.; Leyva, A. *Chem. Commun*., **2003**, 606-607.
36. Vibhute, S. P.; Mhaldar, P. M.; Korade, S. N.; Gaikwad, D. S.; Shejawal, R. V.; Pore, D.M. *Tetrahedron Lett.* **2018**, 59, 3643-3652.
37. Polshettiwar, V.; Varma, R. S. *Org. Biomol. Chem*., **2009**, 7, 37-40.
38. Waldron.; R. D. *Phys. Rev*., **1955**, 99, 1727.
39. Esmaeilpour, M.; Sardarian A. R.; Javidi, J. *J. Organomet. Chem*., **2014**, 749, 233-240.
40. (a) Braga, A. A. C.; Morgon, N. H.; Ujaque G.; Maseras, F. *J. Am. Chem. Soc.*, **2005**, 127, 9298−9307; (b) Sicre, C.; Braga, A. A. C.; Maseras F.; Cid, M. M. *Tetrahedron*, **2008**, 64, 7437–7443; (c) Carrow B. P.; Hartwig, J. F *J. Am. Chem. Soc.,* **2011**, 133, 2116–2119; (d) Amatore, C.; Jutand A.; Le Duc, G. *Chem. Eur. J*., **2011**, 17, 2492-2503.
41. Crowley, B. M.; Potteiger, C. M.; Deng, J. Z.; Prier, C. K.; Paone, D. V.; Burgey, C. S. *Tetrahedron Lett.* **2011**, 52, 5055-5059.
42. Kitamura, Y.; Sako, S.; Udzu, T.; Tsutsui, A.; Maegawa, T.; Monguchi Y.; Sajiki, H. *Chem. Commun.*, **2007**, 5069-5943.
43. Shi S.; Zhang Y., *Green Chem*., **2008**, 10, 868-872.
44. Liu C.; Yang, W. *Chem. Commun*., **2009**, 6267-6272.
45. Rathi, A.K.; Gawande, M.B.; Pechousek, J.; Tucek, J.; Aparicio, C.; Petr, M.; Tomanec, O.; Krikavova, R.; Travnicek, Z.; Varma, R.S.; Zboril, R. *Green Chem*., **2016**, 18, 2363-2373.
46. Lv, G.; Mai, W.; Jin,R.; Gao, L. *Synlett.,*2008, **9**, 1418-1422.
47. Zhang, X.; Li, P.; Ji, Y.; Zhang, L.; Wang, L. *Synthesis*, **2011**,18, 2975–2983
48. Arlin Jose Amali and Rohit Kumar Rana, Green Chem., 2009,11, 1781-1786.
49. Shylesh,S.; Wang, L.; Thiel, W. R. *Adv. Synth. Catal*., **2010**, 352, 425-432.
50. Yang, H.; Wang, Y.; Qin, Y.; Chong, Y.; Yang, Q.; Li, G.; Zhang, L.; Li, W. *Green Chem*., **2011**, 13, 1352-1361.
51. Tanhaei, M.; Mahjoub, A.; Nejat, R. *Catal. Lett*., **2018**, 148, 1549–1561.
52. Sarvi, I. Gholizadeh, M. Izadyar, M. *Catal. Lett.,* **2017**, 147, 1162-1171.
53. Ghorbani-Vaghei, R.; Hemmati, S.; Veisib H.; *J. Mol. Catal. A-Chem*., **2014**, 393, 420-247.

Journal Pre-proofs

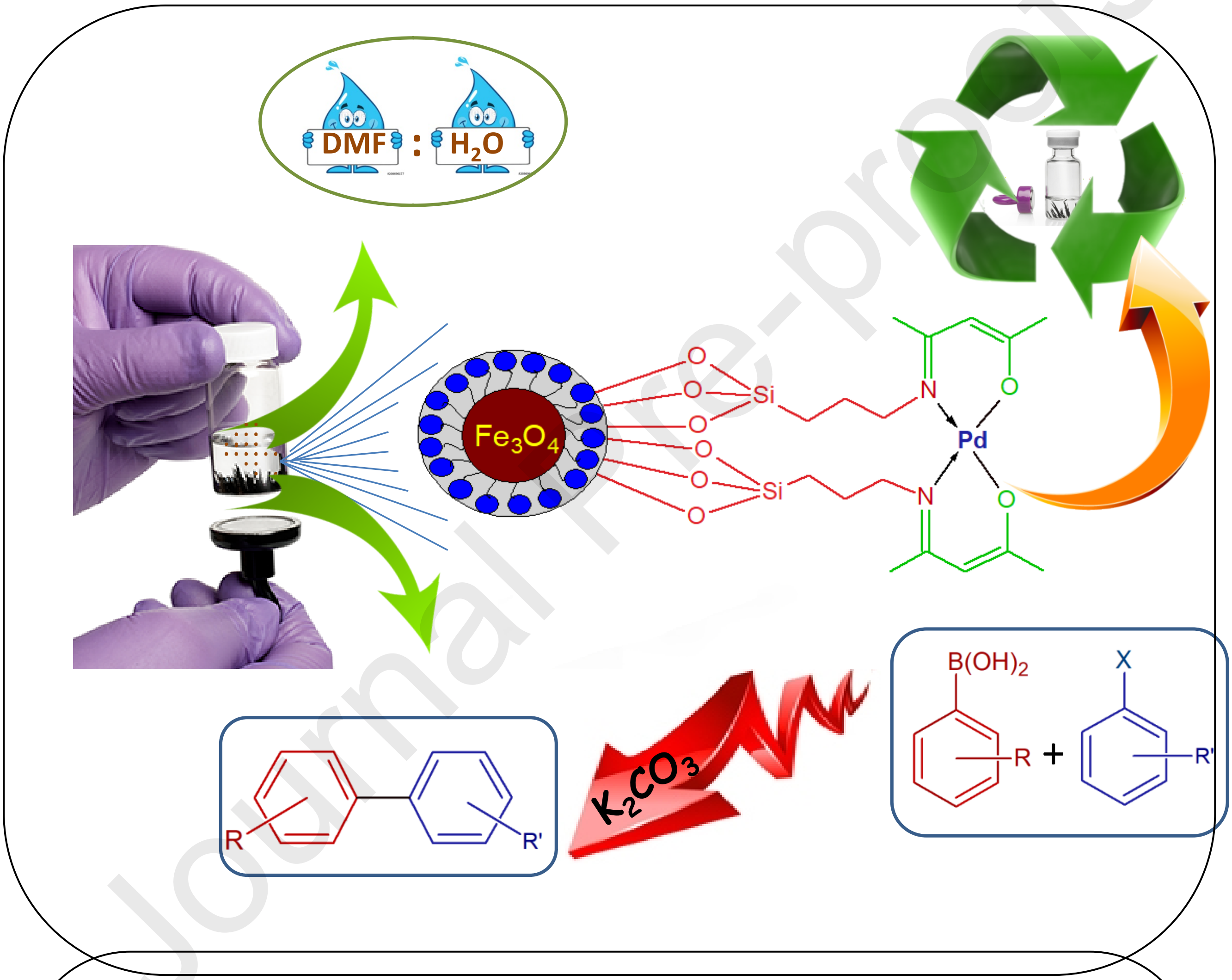
Journal Pre-proofs

Graphical Abstract

Magnetic Nanoparticles-Supported Palladium catalyzed Suzuki-Miyaura Cross Coupling

Sandip P. Vibhute[a,b], Pradeep M. Mhaldar[a], Rajendra V. Shejwal[b], Dattaprasad M. Pore[a*]

[a]*Department of Chemistry, Shivaji University, Kolhapur- 416004, India *E-mail: p_dattaprasad@rediffmail.com*
[b]*Lal Bahadur Shastri College of Arts, Science and Commerce, Satara., India*



Journal Pre-proofs

Highlights

- The functionalized Fe_3O_4 MNPs were synthesized and elucidated by various Characterization techniques.
- Magnetically induced Suzuki-Miyaura cross coupling at ambient condition.
- Low palladium loading was used in the reaction.
- Wide functional group compatibility, moderate to excellent yields, simple workup.

for

several cycles.

SHIVAJI UNIVERSITY, KOLHAPUR
DEPARTMENT OF CHEMISTRY
UGC-SAP AND DST – FIST SPONSORED

Prof. (Dr.) Dattaprasad M. Pore
Professor

Vidyanagar,
Kolhapur-416004,
Maharashtra, INDIA
Phone: (0) (0231) 2609161/9164
Fax: +91-0231-2609000
Email: p_dattaprasad@rediffmail.com

To,

The Editor

Tetrahedron Letters

Manuscript title: “Magnetic Nanoparticles-Supported Palladium catalyzed Suzuki-Miyaura Cross Coupling”

A new magnetic nanoparticles-supported palladium(II) nanomagnetic catalyst (Pd-AcAc-Am-Fe_3O_4@SiO_2) was synthesized and characterized using attenuated total reflectance infrared spectroscopy (ATR-IR), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), energy-dispersive X-ray spectroscopy (EDS), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM). The nanomagnetic catalyst was used as convenient and efficient catalyst for the Suzuki–Miyaura cross-coupling of various aryl bromides/chlorides/iodides with phenylboronic acid. The effects of varying solvents, base, temperature, reaction time and catalyst amount on the performance of the Suzuki– Miyaura cross-coupling reaction were investigated. The notable advantages of this heterogeneous nanomagnetic catalyst are excellent yields, mild reaction conditions, short reaction times and easy magnetic work-up and recyclability. Moreover, the new nanomagnetic catalyst could be easily recovered with an external magnet and could be reused at least six times without significant loss of its catalytic activity.

Thus, we believe this manuscript deserves to be published in “Tetrahedron Letters” and request you to consider our manuscript favorably for publication in your esteemed journal.

Journal Pre-proofs

Journal Pre-proofs

Prof. (Dr.) D. M. Pore

Journal Pre-proofs