

Palladium Loaded on Magnetic Nanoparticles as Efficient and Recyclable Catalyst for the Suzuki- Miyaura Reaction

H. Khojasteh*, V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork

Department of Chemistry, Catalysis Division, University of Isfahan, Isfahan.

Article history:

Received 30/06/2015

Accepted 10/08/2015

Published online 01/09/2015

Keywords:

Magnetic Nanoparticles

Schiff base

Suzuki Reaction

Catalyst Reusability

*Corresponding author:

E-mail address:

hn.khojasteh@sci.ui.ac.ir

Phone: +984435662312

Fax: +984435662312

Abstract

Palladium is the best metal catalyst for Suzuki cross coupling reaction for synthesis of unsymmetrical biaryl compounds. But its high cost limits its application in wide scale. Using of nanoscale particles as active catalytic sites is a good approach for reducing needed noble metal. By loading precious nanoparticles on magnetic nanocores as a support, recycling and reusing of catalyst will be possible. Magnetic nanoparticles have super paramagnetic feature and applying an external magnetic field can collect the supported catalyst from reaction milieu simply. In this work new palladium catalyst immobilized on modified magnetic nanoparticles containing NNO donor atoms were synthesized. Then the catalyst characterized by FT-IR spectroscopy, thermogravimetric analysis, X-ray diffraction and ICP. Prepared catalyst showed high activity in the Suzuki–Miyaura cross-coupling reaction of phenylboronic acid with aryl halides. Activity, Pd loading, reusability and Pd leaching of catalyst were studied. Results showed that the supported catalyst has the advantage to be completely recoverable with the simple application of an external magnetic field.

1. Introduction

Recently the heterogenisation of homogeneous catalysts and investigation of their use in the production of fine chemical synthesis has become a major area of research, the potential for incorporation in continuous reactors and microreactors over homogeneous systems can have positive environmental consequences [1,2]. Interest in catalysis by metal nanoparticles (NPs) is increasing dramatically recently because of

their extraordinary properties [3-6]. Semi-heterogeneous catalysis is a process between homogeneous and heterogeneous catalysis [7].

Among all C-C cross coupling reactions the Suzuki cross-coupling reaction is an increasingly popular approach for the construction of unsymmetrical biaryl compounds since the arylhalides used are environmentally safer than other organometallic reagents [10- 13]. Toxic and expensive homogeneous palladium phosphine

complexes, which are rarely recoverable and impure products [14], are used as the catalysts for the Suzuki reaction [15- 17].

What qualifies as "nanotechnology" today is basic research and development that is happening in laboratories all over the world. Nanoparticles have attracted significant interest as efficient supports for homogeneous catalyst immobilization because of their high surface area [18- 24]. The use of nanoparticles as a support can lead to significant enhancement of catalyst activity, because nanoparticle materials have very small size and are easily dispersed in solution [25, 26]. When the size of the support is decreased to the nanometer scale, the activity of the supported catalyst can be dramatically improved compared to homogeneous catalysts immobilized on conventional supports under conditions where internal diffusion is rate limiting [27, 28]. However, the facile separation and recycling of the nanoparticle materials from the reaction media remains a challenge [27, 29]. The problem can be solved by employing magnetic supports. Catalysts supported magnetic nanoparticles (MNPs) can be readily isolated from the product solution merely by applying an external magnetic field [30, 31].

Current research in our laboratory is directed at the design and immobilization of several catalysts on superparamagnetic nanoparticles for a wide range of organic transformations. Magnetic separation has emerged as a robust, highly efficient and fast separation tool with many advantages compared with product/catalyst isolation by means of other chemical or physical procedures, such as liquid-liquid extraction, chromatography, filtration or centrifugation [32].

In this paper we synthesized a new palladium catalyst immobilized on modified magnetic

nanoparticles containing donor Schiff base ligands. Here, we gathered the advantages of heterogeneous catalysis, thermally stable, oxygen insensitive, air and moisture-stable, magnetic separation and enhanced catalytic activity of palladium without added phosphine ligands to synthesize a new catalyst for Suzuki cross-coupling reaction.

2. Experimental procedure

2.1. Materials

Reactions of catalyst preparing were run under an inert argon or nitrogen atmosphere. polyethylene glycol 400 (PEG 400), Hydrochloric acid, Ammonium hydroxide 30%, DMF, Aryl halides, Toluene, Phenylboronic acid, potassium carbonate, Tripotassium phosphate, 2-Propanol, Palladium(II) acetate, Iron(II) chloride hydrate, iron(III) chloride hydrate, Triethylamine, N-(2-aminoethyl)-3-aminopropyltriethoxysilane (AEAPS), Tetraethyl orthosilicate (TEOS), salicylaldehyde, Ethanol and Methanol were purchased from Merck company and all of them used without further purification. Deionized water was used throughout.

2.2. Methods

Gas chromatography experiments (GC) were performed on an Agilent GC 6890 equipped with a 19096C006 80/100 WHP packed column and a flame ionization detector (FID). FT Infrared (FT-IR) spectra were obtained as potassium bromide pellets in the range of 400–4000 cm^{-1} with a Nicolet-Impact 400D spectrophotometer. X-ray diffraction (XRD) analyses were carried out on a D8 Advanced Bruker instrument using Cu K α radiation ($\lambda=1.5406 \text{ \AA}$). The transmission electron microscopy (TEM) was carried out on a Philips CM10 transmission electron microscope operating at 200 kV. The ICP analyses were carried out by a Perkin-Elmer optima 7300 DV spectrometer. Elemental analysis was performed on a LECO, CHNS-932 analyzer. Thermogravimetric analysis (TGA) were carried out on a Mettler TG50

instrument under air flow at a uniform heating rate of $5\text{ }^{\circ}\text{Cmin}^{-1}$ in the range $25\text{--}800\text{ }^{\circ}\text{C}$.

2.3. Preparation of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles

At the first, magnetic nanoparticles were prepared by chemical co-precipitation of Fe^{3+} and Fe^{2+} ions with a molar ratio of 2:1. Typically, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.838 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2.147 g) were dissolved in 38 mL of degased solution HCl 0.4 molar. Then, this solution was added to 375 mL of degased ammonia 0.7 molar solutions quickly and carefully in one portion while stirring in ultrasound bath. The addition of the base to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ salt solution resulted in the formation of the black precipitate of MNPs immediately that is dispersed in solvent. Stirring in ultrasound bath continued for another 30 min. Black solid collected by magnet and washed with ethanol and distilled water three times. Then the sediment dispersed in 150 ml distilled water. At the second step for synthesis of silica-coated Fe_3O_4 nanoparticles, 50 mL of previous suspension added to a solution of 250 mL 2-Propanol. Then sonicated for 20 min and 11.8 mL PEG 400, 50 mL deionized water and 25 mL ammonium hydroxide 28% were added to it respectively. Then, 3 mL tetraethoxysilane (TEOS) was slowly added. The mixture stirred 24h and finally, silica layer was formed on the surface of magnetite nanoparticles through hydrolysis and condensation of TEOS (Fig 1). The resulting silica-coated Fe_3O_4 nanoparticles were thoroughly washed with ethanol and deionized water in ultrasound bath and collected by magnetic separation, followed by drying at $45\text{ }^{\circ}\text{C}$ under vacuum overnight.

2.4. Preparation of $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2$ nanoparticles

The silica coated superparamagnetic nanoparticles ($\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles) were functionalized with N-(2-aminoethyl)-3-aminopropyltriethoxysilane (AEAPS). $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles (2 g) were dispersed in a solution of dry toluene (100 ml). The suspension was sonicated for 30 min at room temperature. Then 2 ml AEAPS was added and the solution was heated at $70\text{ }^{\circ}\text{C}$ with vigorous stirring for 24 h. The final product was washed with toluene (2×100 ml) and acetone (2×100 ml) by magnetic decantation, and dried at $45\text{ }^{\circ}\text{C}$ under vacuum overnight.

2.5. Synthesis of Schiff base immobilized on modified MNPs

The diamino- functionalized magnetic nanoparticles (0.6 g) were added to round-bottom flask containing absolute ethanol (80 ml). The mixture was sonicated for 10 min and then 10 mmol salicylaldehyde was added to flask. The resulting mixture was sonicated for 15 min, and then stirred for 48 h under nitrogen atmosphere. After that the reaction temperature was promoted to $60\text{ }^{\circ}\text{C}$ slowly and stirring was continued for another 24 h. Production of yellowish precipitation indicates for production of Schiff bases. After that, the reaction mixture was cooled to room temperature and the solid was separated by magnetic decantation. The magnetic precipitations was washed with copious amounts of ethanol and acetone and dried under vacuum at $45\text{ }^{\circ}\text{C}$ to yield the immobilized Schiff base.

Fig. 5 shows FT-IR spectra for $\text{Fe}_3\text{O}_4/\text{SiO}_2$, $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2$ nanoparticles. The significant features in the FT-IR spectrum of the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles (Fig.5 A) were the appearance of a peak near 1035 and 423 cm^{-1} for Si–O stretching and Fe–O stretching vibration at approximately 590 cm^{-1} and the absorption band at approximately 3430 cm^{-1} is due to the stretching of Si–O–H and vibrations of residue OH on the surface of silica coated MNPs. FT-IR spectrum after modification with AEAPTMS, shows peaks near 2900 cm^{-1} due to the –CH₂ and aromatic C–H stretching vibrations and peaks near 1584 and 3288 cm^{-1} are attributed to bending vibration and stretching vibration of N–H bond respectively (Fig.5 B). When surface modified by salicylaldehyde the peak of the imine (C=N) stretching vibration appeared at 1616 cm^{-1} which shows success formation of Schiff bases in FT-IR spectra (Fig.6). In FT-IR spectra for immobilized palladium catalyst on Schiff base, all characteristic peaks exist but imine (C=N) stretching vibration give a small shift in the spectrum of immobilized palladium catalyst compared with Schiff base support. This is probably due to the fact that the chemical environment has been changed by the palladium.

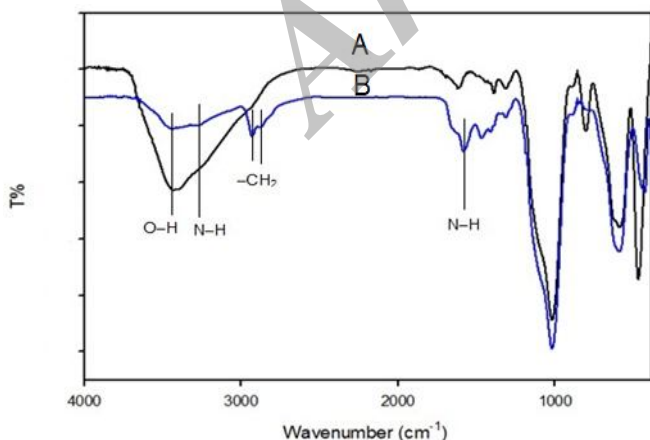


Fig. 5. FT-IR spectra for A: $\text{Fe}_3\text{O}_4/\text{SiO}_2$ and B: $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2$ nanoparticles

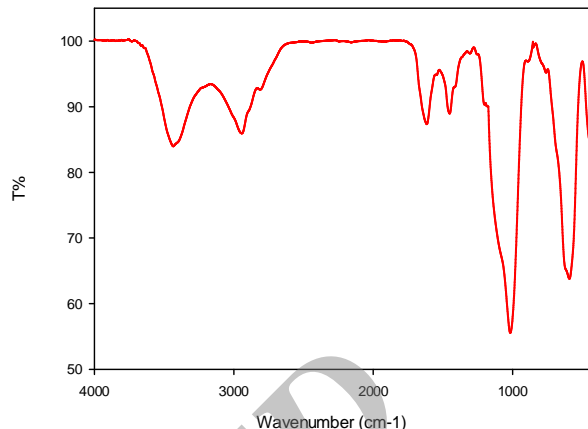


Fig. 6. FT-IR spectra for $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2/\text{SA}$ nanoparticles

To ascertain amount of nitrogen content, elemental analysis (CHNS analysis) performed for $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2$ sample. The results showed 3.31 percent nitrogen content for $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2$. Since each AEAPTMS ligand has two nitrogen atoms so half of this amount shows the amount of stabilised AEAPTMS ligands (Table 1). So the elemental analysis indicated a nitrogen loading of 2.36 mmol/g , corresponding to 1.18 mmol/g of the diamine ligand grafted on the superparamagnetic nanoparticles.

Table 1: Experimental Percent of CHNS elements at CHNS analysis

Sample \ Element	C	H	N	S
$\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2$	11.14	2.80	3.31	---
Standard Deviation (%)	0.05	0.06	0.05	0.01

The TEM image of the as-prepared catalyst is presented in Fig.7. This micrographs show that most of the particles are quasi-spherical and a thin layer of silica coted each of them. The size of these nanoparticles can be estimated from the images of to be in the range of 8-14 nm, which is in a close agreement with the sizes obtained from XRD studies. TEM images of catalysts also show the core-shell

structure of the particles, and the silica coating, which has a uniform thickness of about 5 nm.

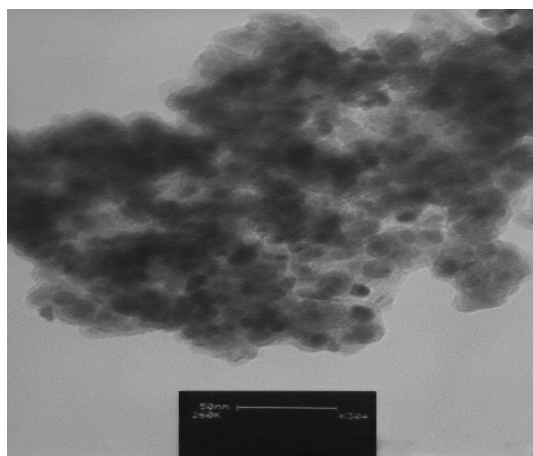


Fig. 7. TEM images of $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2/\text{SA}$ - Pd catalyst

The organic compounds and Pd loading for Schiff bases and catalyst was measured through the TGA runs in the condition of nitrogen atmosphere at the heating rate of $5^\circ\text{C}/\text{min}$ (Fig. 8). Variations of the residual masses of the samples with temperature can be observed. The organic materials and solvents absorbed on the surface of the samples are completely burned to generate gas products at the elevated temperature. The magnetite amounts of the samples and amounts of organic compounds and Pd loading can be estimated from the residual mass percentages (Table 2). Thermo gravimetric charts of Schiff bases pointed that the main mass of catalysts has magnetite contents. The first weight loss stage (below 230°C) is attributed to the evaporation of adsorbed water and solvent molecules on the surface of catalyst, while the other stage beginning at about 260°C was due to the decomposition of AEAPTMS and ligands at elevated temperatures, which can produce metallic cobalt and boron oxide [18].

Table 2. Amount of organic compounds in Schiff bases based on TGA data

Material	Amount of organic compounds %	Amount of Pd loaded (mmol Pd/gr)
$\text{Fe}_3\text{O}_4/\text{SiO}_2$	2%	---
$\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2$	11.2%	---
$\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2/\text{S}$	15.77%	0.45

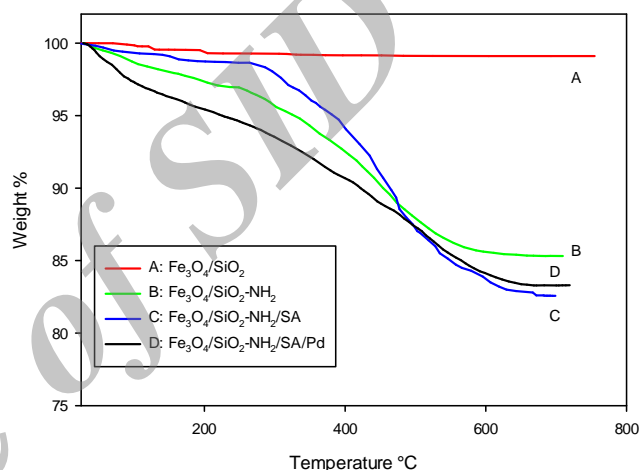


Fig. 8. TGA graphs of the unfunctionalized functionalized, magnetic nanoparticles and immobilized Schiff base ligands and catalyst

The accurate content of palladium in the catalyst determined by inductively - optical emission spectrometry (ICP-OES). Palladium content was $0.342 \text{ mmol Pd g}^{-1}$ of MNPs support. This is another proof for the fact that palladium Nanoparticles was be immobilized onto the Schiff base modified MNPs.

3.2. General procedure for Suzuki reactions

A reaction model consist of iodobenzene and phenylboronic acid in the presence of base in molar ratio of 1:1.2:2 respectively by Pd ($\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2/\text{SA}/\text{Pd}$) in 3 ml of solvent was chosen for optimization of reaction parameters such as the base,

solvent types, temperature and catalyst loading. The reaction mixture was stirred under air atmosphere.

The crude product was quantified by GC analysis. The results are summarized in Table 3-6. Initially the model reaction performed in the presence of different organic and inorganic bases (Table 3). Among them K_3PO_4 was found to be the most effective base for $Fe_3O_4/SiO_2-NH_2/SA/Pd$ catalyst.

Table 3. Effect of different bases on reaction conversion

Base	$Fe_3O_4/SiO_2-NH_2/SA/Pd$ Yield (%) ^a
No base	3
K_2CO_3	74
Na_3PO_4	72
Na_2CO_3	54
Et_3N	21
KOH	60
K_3PO_4	85

^a Reaction conditions: Iodobenzene (1 mmol), Phenylboronic acid (1.2 mmol), Base (2 mmol), $T=75^\circ C$, $t=1h$ and 3 mL of optimized solvent in air.

Table 4. Effect of different solvents on reaction conversion.

Solvent	$Fe_3O_4/SiO_2-NH_2/SA/Pd$ Yield (%) ^a
Ethanol	47
Ethanol/ H_2O (2:1)	54
Methanol	51
Methanol/ H_2O (2:1)	57
DMF	49
DMF/ H_2O (1:1)	55
Toluene	64

^a Reaction conditions: iodobenzene (1 mmol), phenylboronic acid (1.2 mmol), K_3PO_4 (2 mmol), $T=75^\circ C$, $t=1h$ and 3 mL of solvent in air atmosphere

Table 5: Effect of temperature on reaction conversion

Temperature ($^\circ C$)	$Fe_3O_4/SiO_2-NH_2/SA/Pd$ Yield (%) ^a
50	42
60	59
70	62
80	69
100	76
110	79

^a Reaction conditions: iodobenzene (1 mmol), phenylboronic acid (1.2 mmol), optimized base (2 mmol), Cat (1 mol% Pd), $T=75^\circ C$, $t=1h$ and 3 mL of optimized solvent in air atmosphere


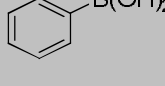
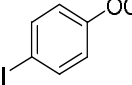
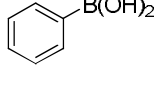
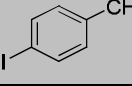
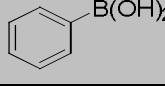
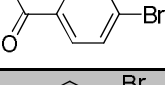
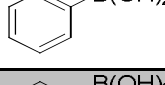

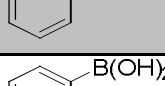
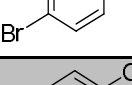
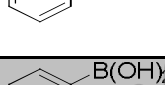
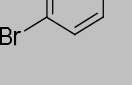


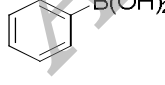
Then, the same reaction was carried out in different single and mixed solvents (Table 4) in presence of optimized base. Among the solvents examined, Toluene achieved better result. The investigation for effect of the temperature on reaction showed that temperature of $100^\circ C$ is best (table 5). The effects of the amount of palladium content on the model reaction were also investigated; the best result for catalyst was obtained using 1.5 mol% Pd. Therefore, it was concluded that the optimum reaction conditions involved arylhalide (1 mmol), phenylboronic acid (1.2 mmol), K_3PO_4 (2 mmol) and catalyst (1.5 mol% Pd) in Toluene at temperature of $100^\circ C$.

3.3. Activating of catalysts in Suzuki reaction

Afterward under the optimized conditions, the immobilized palladium catalysts were assessed for their activity in the Suzuki cross-coupling reaction. Diversity of aryl halides containing electron-donating and electron-withdrawing substituents in presence of Catalyst reacted efficiently with phenylboronic acid under optimized condition and air atmosphere to afford the desired cross-coupling products. The catalyst separation at the end of the reaction was performed exclusively by using a permanent magnet

to recover the catalyst in the reactor wall, taking profit of the composition of the catalyst support that consists of silica-coated magnetite NPs. Such a catalytic support shows excellent magnetic properties to render magnetic separation of catalyst from reaction environment.

Table 6: Activating of Cat ($\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2/\text{SA}/\text{Pd}$) in Suzuki reaction

Arylhalyde	Phenylboronic acid	Time	Yield	TOF
		55	94	68.4
		50	89	71.2
		50	90	72.0
		55	87	63.2
		60	85	56.6
		60	81	54
		60	81	54
		250 ^b	74	11.8

^a Reaction conditions: iodobenzene (1 mmol), phenylboronic acid (1.2 mmol), optimized base (2 mmol), Cat (1 mol% Pd), $T=75^\circ\text{C}$, $t=1\text{h}$ and 3 mL of optimized solvent in air atmosphere

Results for catalyst activity listed at Table 6. As expected, it was observed that the presence of an

electron-withdrawing group on the benzene ring of the aryl halide significantly accelerated the Suzuki reaction, while the presence of an electron-donating group resulted in a significantly drop in reaction rate. Deactivated aryl iodides possessing electron-donating groups showed a slight drop in reactivity compared to those possessing electron-withdrawing groups. However, only a little longer reaction time was required to reach almost quantitative conversion.

3.4. Catalyst recycling

Further investigations were performed to verify the catalyst stability and recyclability in Suzuki reaction. A reaction model containing arylboronide (1 mmol), phenylboronic acid (1.2 mmol), optimized base (2 mmol), Catalyst (1.5 mol% Pd) and 3 mL of optimized solvent in air atmosphere and optimized temperature for this part was chosen. After each run with complete conversion, the catalyst removed easily by external magnet and washed by ethanol water and acetone and then reused in next cycle of catalytic reaction again. Results have been showed in Fig. 9. The catalyst has been reused in model reaction for four reaction cycles. As shown in figure, the yields were above 85% in all reused reaction cycles and the decreased catalytic activity as recycling proceeded may be due to the significant loss of palladium or aggregation of Pd nanoparticles and degrading of surface area of Pd nanoparticles.

3.5. Catalyst leaching

Metal leaching of the catalyst was studied by ICP-OES analysis before and after reaction. The Pd leaching for catalyst after 4 cycle was about 3.8% that confirmed negligible Pd leaching. In addition, by keeping on the reaction with the isolated solution no further reactivity observed.

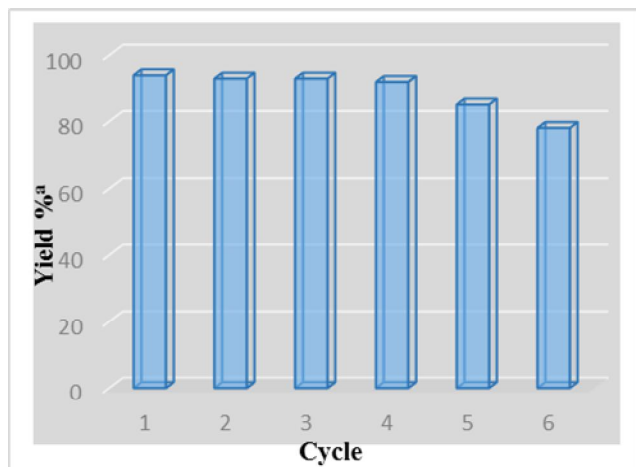


Fig. 9. Recycling experiments for catalyst

4. Conclusions

Tree palladium catalyst immobilized on modified silica coated superparamagnetic nanoparticles was synthesized and characterized. The catalyst was phosphine free ligands and used as catalyst for the Suzuki cross-coupling reaction of several aryl halides with phenylboronic acid. The presence of pendant Schiff base groups on the catalyst support seems to play a special role in the catalytic activity of the Pd NPs, resulting in higher selectivity, conversion and reusability. Amine and oxygen groups are donors and would be stabilize the catalytic active palladium species and thus might explain schiff base function in catalyst. The recovery of the catalyst was easily achieved by simple magnetic decantation using an external magnetic field. The catalyst can be reused several times without significant degradation in catalytic activity. Results for catalyst recycling introduced catalyst as stable and recyclable catalyst for this reaction. Amount of Pd leached for catalyst was negligible that maybe hexagonal space and donor atoms make surface of catalyst suitable for translocation of Pd nanoparticles.

Acknowledgements

Authors are grateful to the council of University of Isfahan for providing financial support to undertake this work.

References

- [1] J.H. Clark, D.J. MacQuarrie, J.H. Clark, D.J. MacQuarrie, *Handbook of Green Chemistry & Technology*, Blackwell, Oxford, 2002.
- [2] P.T. Anastas, M.M. Kirchhoff, T.C. Williamson, *Applied Catalysis A: General* 221 (2001) 3-13.
- [3] S. Miao, C. Zhang, Z. Liu, B. Han, Y. Xie, S. Ding, Z. Yang, *The Journal of Physical Chemistry C* 112 (2008) 774-780.
- [4] C.W. Lim, I.S. Lee, *Nano Today* 5 (2010) 412-434.
- [5] A. Fihri, M. Bouhrara, B. Nekoueishahraki, J.-M. Basset, V. Polshettiwar, *Chem Soc Rev.* 40 (2011) 5181-5203.
- [6] G.R. Bardajee, R. Malakooti, I. Abtin, H. Atashin, *Microporous and Mesoporous Materials* 169 (2013) 67-74.
- [7] D. Astruc, F. Lu, J.R. Aranzas, *Angew Chem Int Ed Engl*, 44 (2005) 7852-7872.
- [8] S. Paul, J.H. Clark, *Green Chemistry* 5 (2003) 635-638.
- [9] K.C. Nicolaou, E.J. Sorensen, Wiley-VCH, Weinheim 1996.
- [10] Á. Molnár, *Chemical Reviews* 111 (2011) 2251-2320.
- [11] R. Narayanan, *Molecules* 15 (2010) 2124.
- [12] A. Fihri, M. Bouhrara, B. Nekoueishahraki, J.-M. Basset, V. Polshettiwar, *Chem Soc Rev* 40 (2011) 5181-5203.
- [13] N. Miyaura, A. Suzuki, *Chemical Reviews* 95 (1995) 2457-2483.
- [14] Y. He, C. Cai, *Catalysis Communications* 12 (2011) 678-683.
- [15] F. Bellina, A. Carpita, R. Rossi, *Synthesis* 15 (2004) 2419-2440.

- [16] N.T.S. Phan, C.S. Gill, J.V. Nguyen, Z.J. Zhang, C.W. Jones, *Angewandte Chemie International Edition* 45 (2006) 2209-2212.
- [17] J.-P. Corbet, G. Mignani, *Chemical Reviews* 106 (2006) 2651-2710.
- [18] J. Wu, P. Su, J. Huang, S. Wang, Y. Yang, *J Colloid Interface Sci* 399 (2013) 107-114.
- [19] B. Tamami, H. Allahyari, S. Ghasemi, F. Farjadian, *Journal of Organometallic Chemistry* 696 (2011) 594-599.
- [20] N.T.S. Phan, H.V. Le, *Journal of Molecular Catalysis A: Chemical* 334 (2011) 130-138.
- [21] P. Das, D. Sharma, A.K. Shil, A. Kumari, *Tetrahedron Letters* 52 (2011) 1176-1178.
- [22] N.T. Bui, T.B. Dang, H.V. Le, N.T.S. Phan, *Chinese Journal of Catalysis* 32 (2011) 1667-1676.
- [23] P. Wang, Q. Lu, J. Li, *Materials Research Bulletin* 45 (2010) 129-134.
- [24] G. Fan, B. Zou, S. Cheng, L. Zheng, *Journal of Industrial and Engineering Chemistry* 16 (2010) 220-223.
- [25] M. Kooti, M. Afshari, *Catal Lett* 142 (2012) 319-325.
- [26] S. Paul, J.H. Clark, *Journal of Molecular Catalysis A: Chemical* 215 (2004) 107-111.
- [27] N.T.S. Phan, C.W. Jones, *Journal of Molecular Catalysis A: Chemical* 253 (2006) 123-131.
- [28] Y. W, M.S. M, PanZ, O.S. H, D. S, *Journal of the American Chemical Society* 127 (2005) 10480-10481.
- [29] D. Astruc, F. Lu, J.R. Aranzaes, *Angew Chem Int Ed Engl* 44 (2005) 7852-7872.
- [30] C.W. Lim, I.S. Lee, *Nano Today* 5 (2010) 412-434.
- [31] N.T.S. Phan, C.S. Gill, J.V. Nguyen, Z.J. Zhang, C.W. Jones, *Angewandte Chemie International Edition* 45 (2006) 2209-2212.
- [32] N.J.S. Costa, P.K. Kiyohara, A.L. Monteiro, Y. Coppel, K. Philippot, L.M. Ross, *Journal of Catalysis* 276 (2010) 382-389.
- [33] V.M. Nosova, Y.A. Ustynyuk, L.G. Bruk, O.N. Temkin, A.V. Kisin, P.A. Storozhenko, *Inorg Chem* 50 (2011) 9300-9310.