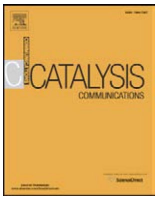
Catalysis Communications 12 (2011) 678–683

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom



Short Communication

Polymer-supported macrocyclic Schiff base palladium complex: An efficient and reusable catalyst for Suzuki cross-coupling reaction under ambient condition

Ying He, Chun Cai *

Chemical Engineering College, Nanjing University of Science & Technology, Nanjing 210094, PR China

ARTICLE INFO

Article history:
Received 8 October 2010
Received in revised form 10 December 2010
Accepted 13 December 2010
Available online 20 December 2010

Keywords:
Polymer-supported palladium complex
Macrocyclic Schiff base
Heterogeneous catalysis
Suzuki cross-coupling reaction

ABSTRACT

Polymer-supported macrocyclic Schiff base palladium complex was prepared and characterized. The catalyst exhibits excellent catalytic activity and stability for Suzuki cross-coupling reaction under ambient condition. Various aryl bromides were coupled with aryl boronic acids in DMF/H_2O, under air, in the presence of 0.1 mol% of the catalyst to afford corresponding cross-coupled products in high yields within 20–30 min. Furthermore, the heterogeneous catalyst can be readily recovered by simple filtration and reused several times without significant loss in its activity.

1. Introduction

Transition metal-catalyzed cross-coupling reactions have been recognized as powerful synthetic tools and a major area of interest in multiple organic transformations for academic and industrial processes [1]. In particular, the Suzuki cross-coupling reaction, which is the palladium-catalyzed cross-coupling of organic halides with aryl boronic acids, is one of the most important methods of forming C–C bonds in synthetic chemistry, and finds important industrial applications [2–8].

In recent years, great efforts in catalysis research have been devoted to the introduction and application of effective and safe heterogeneous catalysts. Polymers play a significant role in this area offering different ways of metal attachment to the polymer matrix via covalent or non-covalent bonding, through hydrogen bridges, as well as through ionic, hydrophobic or fluorous interactions [9]. Correspondingly, palladium complexes anchored on polymers with Schiff bases [10,11], N-heterocyclic carbene groups [12–15], and dendrimers [16,17] have been described recently. In addition, a few efficient heterogeneous Pd catalysts, which are of general use for this reaction of aryl chlorides, have also been reported [18–25].

Schiff bases are an important class of ligands in coordination chemistry and have studied extensively [26] as they are selective and sensitive toward various metal ions. However, the use of metal Schiff base complexes as catalyst in homogeneous solution often suffers from deactivation due to easy formation of dimeric peroxo- and μ-oxo species, which have been demonstrated to be inactive in various catalytic reactions [27–29]. Moreover, homogeneous processes suffer from the problems concerning separation from reaction mixture, reuse of expensive metal catalysts and metal contamination in the products. In order to overcome these drawbacks, immobilization via covalent bond on the support is more advantageous over conventional impregnation in terms of minimizing catalyst leaching and improving the long-term stability of the solid catalyst. As for generation of the C–C bonds, Li and co-workers have reported the use of poly (vinyl chloride) supported Schiff base nano-palladium complex for Suzuki cross-coupling reaction efficiently [30]. Homogeneous palladium non-symmetrical salen-type Schiff base complexes have been prepared and shown to be effective in the heterogeneous catalysis of C–C cross-coupling reactions [31]. However, most of the supported Schiff base palladium complexes used as promoter in the Suzuki reaction is either longer reaction time or heating required. In continuation of our studies in developing new functional supported catalysts, herein we reported an efficient and widely applicable approach for the preparation of chloromethylated polystyrene resin supported macrocyclic Schiff base palladium complex and their application as heterogeneous catalyst in Suzuki cross-coupling reaction under ambient condition (Scheme 1).

2. Experimental

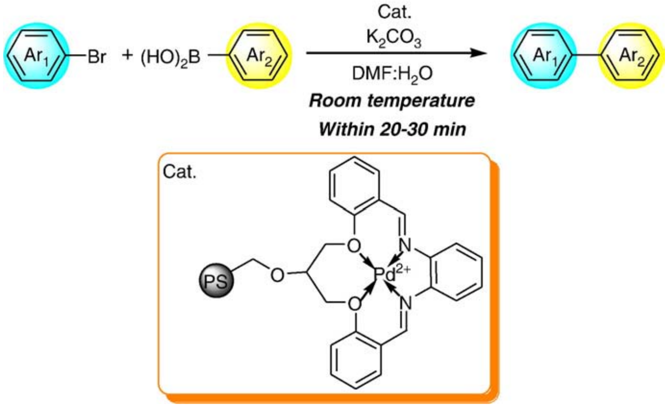
2.1. General remarks

All chemicals were reagent grade and used as purchased. Chloromethylated polystyrene resin (1% divinylbenzene, 1.0 mmol/g of Cl, grain size range: 100–200 mesh) was obtained from GL Biochem

---

* Corresponding author. Tel.: +86 25 84315514; fax: +86 25 84315030.
E-mail address: c.cai@mail.njust.edu.cn (C. Cai).

1566-7367/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2010.12.017



Scheme 1. Polymer-supported macrocyclic Schiff base palladium complex for Suzuki cross-coupling reaction.

(Shanghai) Ltd. (Shanghai, China). IR spectra were recorded in KBr disks with a SHIMADZU IRPrestige-21 FT-IR spectrometer. Elemental analyses were performed on a Vario ELIII recorder. Scanning electron microscopy (SEM) analyses were performed with JEOL JSM-6380LV instrument. Transmission electron microscopy (TEM) images were performed with a JEM-2100 instrument. ^{1}H NMR spectra were measured with a Bruker Avance III 500 analyzer. GC–MS analyses were performed on a Saturn 2000GC/MS instrument. Palladium content of the catalyst was measured by inductively coupled plasma (ICP) on PE5300DV analyzer.

2.2. Preparation of catalyst

2.2.1. Preparation of 2-[3-(2-formylphenoxy)-2-hydroxypropoxy] benzaldehyde

2-[3-(2-Formylphenoxy)-2-hydroxypropoxy] benzaldehyde was performed according to the literature method [32]. Salicylaldehyde (0.11 mol, 11.36 g) was added to 100 ml of aqueous sodium hydroxide (0.11 mol, 4.4 g) and heated to 60 °C under nitrogen atmosphere. Then, epichlorohydrin (0.05 mol, 4.36 g) was added dropwise within 2 h. The mixture was stirred continuously for another 4 h. After cooling to room-temperature, the yellow precipitate was filtrated off, washed with water for several times, and dried under vacuum. It was recrystallized with methanol/water (8:1, v/v) affording yellow oil solid, and then several portion of water was added to afford the desired product to yield of 34%.

2.2.2. Preparation of polymer supported macrocycle Schiff base

The preparation of the polymer supported Schiff base was modified from the literature methods [32,33]. Pre-washed chloromethylated polystyrene resin 1.0 g (1.0 mmol Cl) was allowed to swell in DMF (15 ml) for 24 h. Then, 2-[3-(2-formylphenoxy)-2-hydroxypropoxy] benzaldehyde (1.5 mmol, 0.45 g), K_2CO_3 (0.276 g, 2.0 mmol), and 18-crown-6 (0.053 g, 0.2 mmol) were added in the mixture. The mixture was stirred at 100 °C for 24 h. The polymer beads were filtered, washed with distilled water, dichloromethane and ethanol and then dried in vacuo. After that, the beads obtained were swollen in methanol (5 ml) for 2 h, and a solution of *o*-phenylene diamine (1.0 mmol, 0.108 g) and a drop of concentrated HCl were added. The contents were refluxed for 24 h. The color of the polymer beads changed from white to pale yellow, indicating attachment of *o*-phenylene diamine. The beads were filtered, washed with distilled water, dichloromethane and methanol, and then dried in vacuo. The formation of macrocycle Schiff base of the polymer resin was confirmed using analytical and infrared (IR) spectral data. The macrocycle Schiff base content of the functional beads was 0.68 mmol/g according to the result of elemental analyses based on N elemental.

2.2.3. Preparation of the catalyst

The functional beads (0.35 g) were swollen in toluene (10 ml) for about 2 h. To this was added $Pd(OAc)_2$ (0.25 mmol, 0.056 g) and the mixture was stirred at 90 °C for about 12 h. Then the resulting beads were filtrated and washed with methanol, dried at 100 °C under vacuum overnight. The content of palladium was 5.8% as determined by ICP.

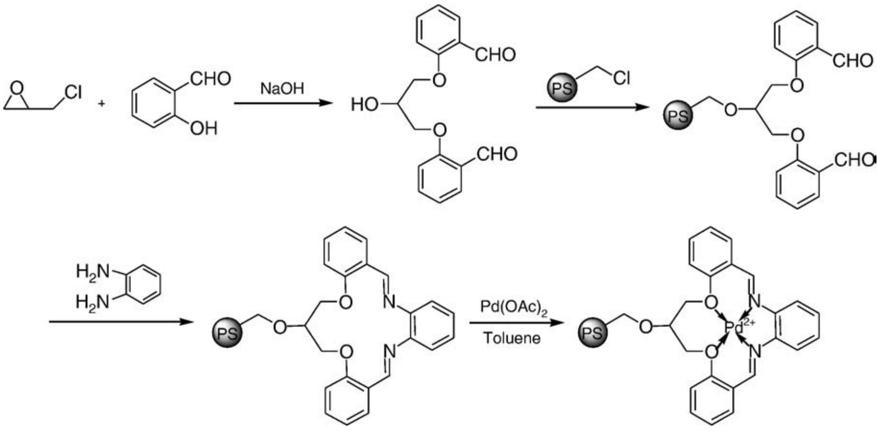
2.3. General procedure for Suzuki cross-coupling reaction

Under air atmosphere, around-bottomed flask was charged with aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), DMF/H_2O (1:1) (6 ml) and catalyst (0.1 mol%). The mixture was reacted for a certain time (monitored by GC). After the reaction completed, water (10 ml) and ether (20 ml) were added. The catalyst was separated by filtration, washed with ether and water, and dried under vacuum for the next cycle. The organic phase of filtrate was separated, dried over Na_2SO_4, and evaporated. The crude product obtained was purified by flash chromatography with n-hexane/EtOAc as eluent to afford the corresponding products.

3. Results and discussion

3.1. Synthesis and characterization of the palladium catalyst

The complex has a macrocyclic structure with palladium as the central metal atom with the corners being occupied by two nitrogen atoms and two oxygen atoms, and it was designed by the sequence of reactions given in Scheme 2. In order to ascertain the functionalized polymer and its corresponding Pd complex, IR spectra were



Scheme 2. Preparation of polymer-supported macrocyclic Schiff base palladium complex.

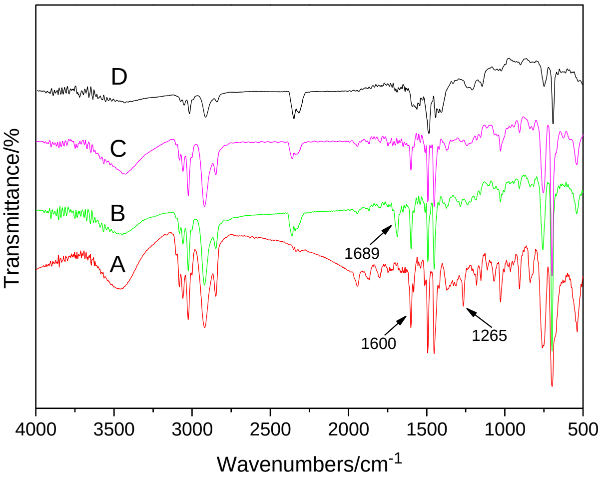


Fig. 1. IR spectra of chloromethylated polystyrene resin (A), polymer-supported 2-[3-(2-formylphenoxy)-2-hydroxypropoxy] benzaldehyde (B), polymer-supported macrocyclic Schiff base (C), and polymer-supported macrocyclic Schiff base palladium complex (D).

recorded separately at different stage of preparation. It can be seen from Fig. 1, the spectrum of chloromethylated polystyrene resin shows an absorption band at 600 and 1265 cm^{-1}, which is attributed to the C–Cl bond, was weakened after the introduction of 2-[3-(2-formylphenoxy)-2-hydroxypropoxy] benzaldehyde. Correspondingly, a strong band at 1689 cm^{-1} in curve B was assigned to the C═O vibration. Moreover, a bond at 1689 cm^{-1} disappeared in curve C after the introduction of *o*-phenylene diamine. The range of 1600–1500 cm^{-1} corresponds to the $\upsilon(C{=}C)$ and $\upsilon(C{=}N)$ stretch of aromatic rings [11]. In the polymer-supported palladium complexes, both υ_{Ar-O-C} and $\upsilon_{C=N}$ undergo a slight positive shift indicating that the palladium is chelated with the nitrogen and oxygen atom.

Then, scanning electron micrograph (SEM) was also recorded to understand morphology of the surface of the support and catalyst. It can be easily seen from Fig. 2; the resin beads have different size and roughness. The presence of Pd caused changes, demonstrated by polymer particle size decrease and roughness of the surface (Fig. 2).

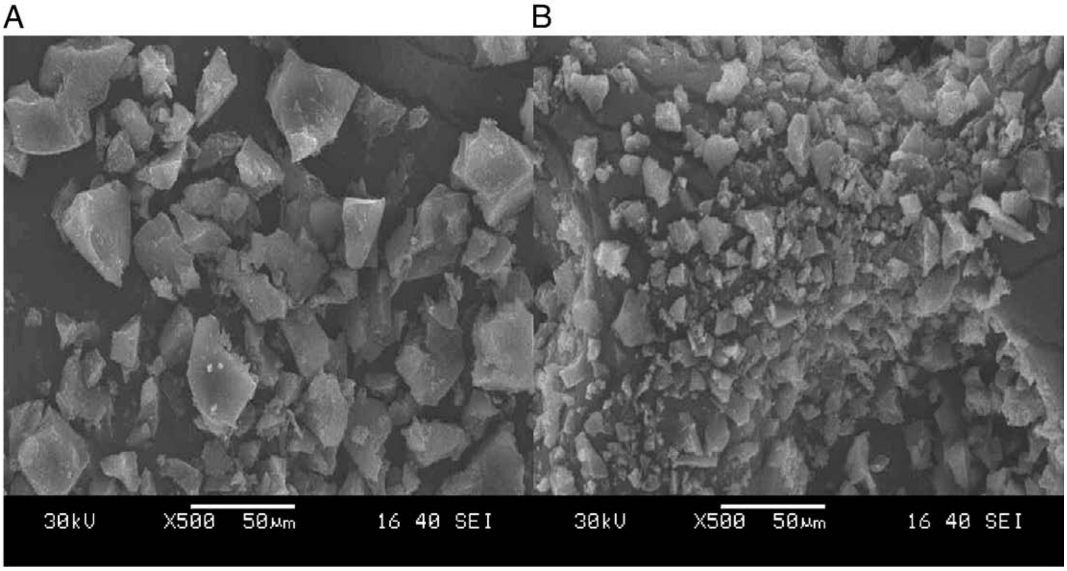
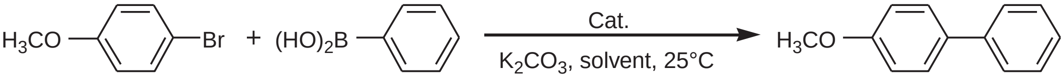


Fig. 2. SEM images of (A) polymer-supported macrocyclic Schiff base; and (B) the fresh palladium catalyst.

Table 1
Effect of solvents for the Suzuki reaction[a].



Entry	Solvent	Time (h)	Yield (%)[b]	TON	TOF (h^{-1})
1	DMF	1	28	280	280
2	EtOH	0.5	62	620	1240
3	CH_3CN	1	6	60	60
4	Toluene	1	32	320	320
5	THF	1	3	30	30
6	H_2O	6	56	560	93.3
7	EtOH/H_2O (v/v = 1:1)	0.5	93	930	1860
8	DMF/H_2O (v/v = 1:1)	0.5	98	980	1960
9	EtOH/H_2O (v/v = 1:2)	0.5	57	570	1140
10	EtOH/H_2O (v/v = 2:1)	0.5	78	780	1560
11	DMF/H_2O (v/v = 1:2)	0.5	83	830	1660
12	DMF/H_2O (v/v = 2:1)	0.5	80	800	1600

[a] Reaction conditions: *p*-bromoanisole (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol); catalyst (0.1 mol%) in 6 ml solvent at room-temperature in air.
[b] Isolated yield.

3.2. Catalytic activity of the catalyst in Suzuki cross-coupling reaction

To check the potency of chloromethylated polystyrene resin supported macrocyclic Schiff base palladium catalyst, it was used in Suzuki cross-coupling reaction. The coupling between *p*-bromoanisole and phenylboronic acid was chosen as model reaction. Initially, the single solvent such as DMF, EtOH, CH_3CN, toluene, THF, and H_2O was studied. As could be seen in Table 1, the single solvents gave low to moderate yields for the reaction at the room-temperature (Table 1, entries 1–6). However, when we adopted the organic/aqueous co-solvent, high yields of 93% to 98% were obtained with high turnover number (TON) and turnover frequency (TOF) (Table 1, entries 7 and 8). The merit of the co-solvent may be attributed to the good solubility of the organic reactants and the inorganic base. Then, we tested the influence of different volume ratios of DMF/H_2O and EtOH/H_2O as a solvent under the Suzuki reaction at room-temperature. Yields of 57–83% were obtained as demonstrated in Table 1, entries 9–12.

Next, we examined the effects of bases on the room-temperature Suzuki reaction in DMF/H_2O. The inorganic bases including K_3PO_4, K_2CO_3, Na_2CO_3, $NaHCO_3$, NaOAc and KF were investigated (Table 2, entries 1–6). As shown in Table 2, K_2CO_3 was the best base for the reaction with high TON 980 and TOF 1960 h^{-1}. Also, the organic base NEt_3 was studied but unsatisfied yield was obtained (Table 2, entry 7). Then, different catalyst loadings were tested for the reaction. As illustrated in Table 2, 0.01 mol% of catalyst gave rise to extremely high TON 8600 and TOF 17,200 h^{-1} (Table 2, entry 9) but lower yield

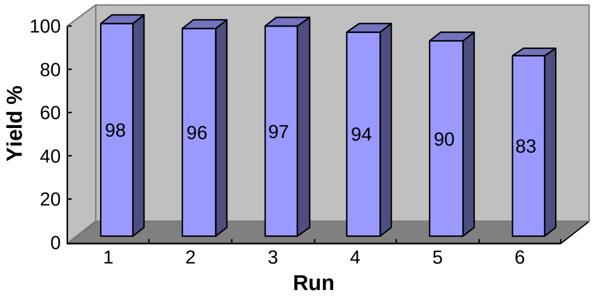
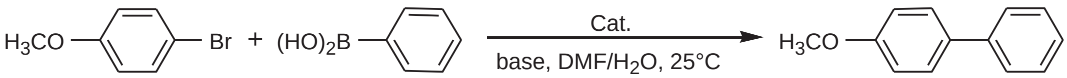


Fig. 3. Recycling experiment.

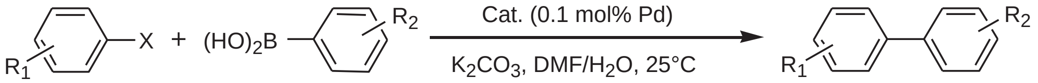
Table 2
Effect of bases and catalyst loadings for the Suzuki cross-coupling reaction[a].



Entry	Catalyst loading (mol%)	Base	Time (h)	Yield (%)[b]	TON	TOF (h^{-1})
1	0.1	K_3PO_4	0.5	96	960	1920
2	0.1	K_2CO_3	0.5	98	980	1960
3	0.1	Na_2CO_3	0.5	91	910	1820
4	0.1	NaOAc	0.5	18	180	360
5	0.1	$NaHCO_3$	0.5	51	510	1020
6	0.1	KF	0.5	45	450	900
7	0.1	NEt_3	1	26	260	260
8	0.5	K_2CO_3	0.5	98	196	392
9	0.01	K_2CO_3	0.5	86	8600	17,200

[a] Reaction conditions: *p*-bromoanisole (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol); catalyst in 6 ml DMF/H_2O (1:1) at room-temperature in air.
[b] Isolated yield.

Table 3
Suzuki cross-coupling reaction of aryl halides with aryl boronic acids[a].



Entry	X	R_1	R_2	Time (min)	Yield (%)[b]	TON	TOF (h^{-1})
1	Br	H	H	30	99	990	1980
2	Br	*p*-NO_2	H	20	99	990	2970
3	Br	*p*-CH_3	H	30	97	970	1940
4	Br	*p*-CH_3O	H	30	98	980	1960
5	Br	*p*-CF_3	H	20	99	990	2970
6	Br	*p*-CH_3CO	H	20	98	980	2940
7	Br	*p*-CHO	H	20	99	990	2970
8	Br	*m*-CF_3	H	20	96	960	2880
9	Br	*o*-CH_3O	H	30	90	900	1800
10	Br	H	*p*-Cl	30	95	950	1900
11	Br	H	*p*-CF_3	30	98	980	1960
12	Br	H	*p*-CH_3	30	93	930	1860
13	Br	H	*p*-CH_3O	30	92	920	1840
14	Cl	*p*-NO_2	H	180	16[c]	160	53.3
15	Cl	*p*-CF_3	H	180	9[c]	90	30

[a] Reaction conditions: aryl halides (1.0 mmol), aryl boronic acids (1.5 mmol), K_2CO_3 (2.0 mmol); catalyst (0.1 mol%) in 6 ml DMF/H_2O (1:1) at room-temperature in air.
[b] Isolated yield.
[c] At 50 °C for 180 min.

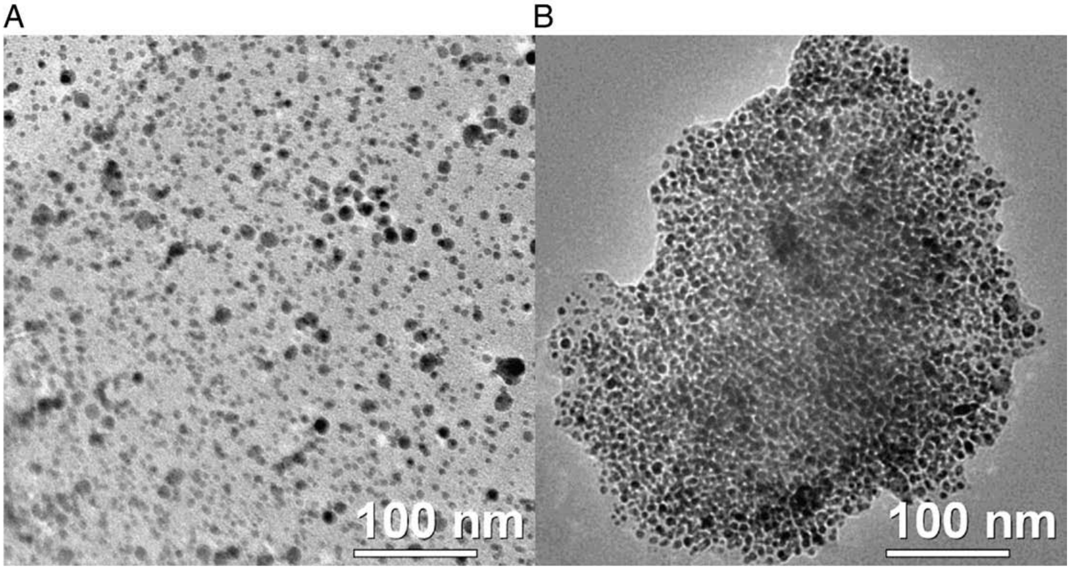


Fig. 4. TEM images of (A) recovered catalyst after first run for the Suzuki reaction; and (B) recovered catalyst after sixth run for the Suzuki reaction.

obtained. Thus, we selected K_2CO_3 as the base, DMF/H_2O in ratio of 1:1 as solvent, and 0.1 mol% of catalyst as the optimal conditions for the reaction.

Encouraged by the efficiency of the reaction protocol described above, we investigated the substrate scope. As shown in Table 3, a wide range of functional groups have also been tolerated in the reaction. The coupling between aryl bromides and phenylboronic acid, which contained electron-donating as well as electron-withdrawing groups, proceeded readily to afford the corresponding products in 90%–99% yields with high TOF (up to 2970 h^{-1}). Meanwhile, the coupling reaction could be efficiently executed of aryl boronic acids with electron-withdrawing or electron-donating groups. Then, we tried to examine whether aryl chlorides were active for the Suzuki reaction. However, poor yields were obtained even for a prolonged time at 50 °C (Table 3, entries 14 and 15).

3.3. Catalyst reusability

The reusability of the catalyst is a very important theme and makes them useful for commercial applications. At this point, the recovery and reusability of the catalyst have been investigated using *p*-bromoanisole with phenylboronic acid as model substrates. As expected, the catalyst showed good reusability with a slight decrease in its activity (Fig. 3) and the yields are 98%, 96%, 97%, 94%, 90% and 83%; however, 1 h and 2 h reaction time was required to runs 3, 4, and runs 5, 6, respectively (TOF values drop from 2970 h^{-1} to 415 h^{-1}). The ICP analysis shows that palladium content of the catalyst doesn't change after catalysis, indicating that no significant leaching of palladium to the solution occurs during the catalytic processions. It's believed that the amount of Pd leaching of the catalyst during the reaction was not a key factor in decreasing the catalytic activity. The TEM analysis of the structure of the catalyst refers to that the Pd of the catalyst after the cross-coupling reaction was in nanoparticle size and shape. Meanwhile, it was found that the size of the palladium (0) nanoparticles inside the beads had increased from 2–5 nm to 20–30 nm after the first run and sixth run (Fig. 4). Therefore, it was reasoned that the slight decrease in catalytic activity in subsequent runs may be due to the passivation of nanoclusters surface [34]. A longer reaction time was used to compensate for the decreased activity, resulting in an increase in coupling yield. Moreover, the filtrate obtained from the filtration of the catalyst after catalysis doesn't show any catalytic activity.

4. Conclusions

In summary, we have successfully prepared polymer supported macrocyclic Schiff base palladium complex which was used as heterogeneous catalyst for the room-temperature Suzuki cross-coupling reaction. The catalyst has showed highly catalytic activities for the reaction affording a diverse range of biphenyls in excellent yields within 20–30 min, and could be easily recovered by simple filtration and reused for 5 times without significant loss in its activity. The excellent catalytic efficiency as well as the recyclability made them an attractive alternative to the large number of heterogeneous palladium catalysts reported to date.

References

[1] I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009–3066.
[2] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457–2483.
[3] A. Suzuki, J. Organomet. Chem. 576 (1999) 147–168.
[4] A. Suzuki, J. Organomet. Chem. 653 (2002) 83–90.
[5] S.P. Stanforth, Tetrahedron 54 (1998) 263–303.
[6] A.F. Littke, G.C. Fu, Angew. Chem. Int. Ed. 41 (2002) 4176–4211.
[7] S. Kotha, K. Lahiri, D. Kashinath, Tetrahedron 58 (2002) 9633–9695.
[8] M. Choi, D.H. Lee, K. Na, B.W. Yu, R. Ryoo, Angew. Chem. Int. Ed. 48 (2009) 3673–3676.
[9] V. Andrushko, D. Schwinn, C.C. Tzschucke, F. Michalek, J. Horn, C. Mossner, W. Bannwarth, Helv. Chim. Acta 88 (2005) 936–949.
[10] C. Gonzalez-Arellano, A. Corma, M. Iglesias, F. Sanchez, Adv. Synth. Catal. 346 (2004) 1316–1328.
[11] Y. Li, X. Fu, B. Gong, X. Zou, X. Tu, J. Chen, J. Mol. Catal. A: Chem. 322 (2010) 55–62.
[12] J.W. Byun, Y.S. Lee, Tetrahedron Lett. 45 (2004) 1837–1840.
[13] P.G. Steel, C.W.T. Teasdale, Tetrahedron Lett. 45 (2004) 8977–8980.
[14] J.H. Kim, J.W. Kim, M. Shokouhimehr, Y.S. Lee, J. Org. Chem. 70 (2005) 6714–6720.
[15] J.W. Kim, J.H. Kim, D.H. Lee, Y.S. Lee, Tetrahedron Lett. 47 (2006) 4745–4748.
[16] J.C. Garcia-Martinez, R.W.J. Scott, R.M. Crooks, J. Am. Chem. Soc. 125 (2003) 11190–11191.
[17] R. van Heerbeek, P.C.J. Kamer, P. van Leeuwen, J.N.H. Reek, Chem. Rev. 102 (2002) 3717–3756.
[18] K. Inada, N. Miyaura, Tetrahedron 56 (2000) 8661–8664.
[19] C.A. Parrish, S.L. Buchwald, J. Org. Chem. 66 (2001) 3820–3827.
[20] K. Glegola, E. Framery, K.M. Pietrusiewicz, D. Sinou, Adv. Synth. Catal. 348 (2006) 1728–1733.
[21] W.J. Sommer, M. Weck, Adv. Synth. Catal. 348 (2006) 2101–2113.
[22] R.B. Bedford, S.J. Coles, M.B. Hursthouse, V.J.M. Scordia, Dalton Trans. (2005) 991–995.
[23] A. Leyva, H. García, A. Corma, Tetrahedron 63 (2007) 7097–7111.
[24] T.J. Colacot, W.A. Carole, B.A. Neide, A. Harad, Organometallics. 27 (2008) 5605–5611.
[25] S. Schweizer, J.-M. Becht, C. Le Drian, Tetrahedron 66 (2010) 765–772.
[26] G. Shing, Ph.A. Shing, A.K. Sen, K. Shing, S.N. Dubey, R.N. Handa, J. Choi, Synth. React. Inorg. Met. Org. Chem. 32 (2002) 171–187.

[27] J.P. Collman, V.J. Lee, C.J. Kellen-Yuen, X. Zhang, J.A. Ibers, J.I. Brauman, J. Am. Chem. Soc. 117 (1995) 692–703.
[28] K.J. Ballus Jr., A.K. Khanmamedova, K.M. Dixon, F. Bedioui, Appl. Catal. A Gen. 143 (1996) 159–173.
[29] C. Heinrichs, W.F. Holderich, Catal. Lett. 58 (1999) 75–80.
[30] J. Liu, Y.Q. Li, W.J. Zheng, Monatsh. Chem. 140 (2009) 1425–1429.
[31] N.T.S. Phan, D.H. Brown, H. Adams, S.E. Spey, P. Styring, Dalton Trans. (2004) 1348–1357.
[32] Y. Chang, X.L. Shi, D.M. Zhu, Y. Liu, Polym. Adv. Technol. 19 (2008) 877–881.
[33] K.C. Gupta, A.K. Sutar, C.C. Lin, Coord. Chem. Rev. 253 (2009) 1926–1946.
[34] T.J. Clark, G.R. Whittell, I. Manners, Inorg. Chem. 46 (2007) 7522–7527.