Palladium(0) nanoclusters stabilized by poly(4-styrenesulfonic acid-co-maleic acid) as an effective catalyst for Suzuki–Miyaura cross-coupling reactions in water

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ABSTRACT

Palladium(0) nanoclusters stabilized by poly(4-styrenesulfonic acid-co-maleic acid), PSSA-co-MA, were generated in situ during the hydrolysis of ammonia–borane (AB) from the reduction of potassium tetrachloropalladate(II) in aqueous solution at room temperature. They were isolated from the reaction solution and characterized by UV–visible electronic absorption spectroscopy, TEM, SAED and XRD techniques. The PSSA-co-MA stabilized palladium(0) nanoclusters were used as catalyst in Suzuki–Miyaura cross-coupling reactions of various of arylbromides or aryl iodide with phenylboronic acid in water without any purification process after catalytic hydrolysis of AB. They show excellent catalytic activity in coupling of series of aryl bromides or aryl iodide with phenylboronic acid under the optimized reaction conditions in water. PSSA-co-MA stabilized palladium(0) nanoclusters provided turnover frequency of 1980 and 5940 h^{-1} in Suzuki–Miyaura coupling reactions of phenylboronic acid with p-bromoacetophenone or p-iodobenzene, respectively, which are the highest values ever reported for the Suzuki–Miyaura coupling reactions in water as sole solvent.

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1. Introduction

The Suzuki–Miyaura cross-coupling reaction of aryl halides with arylboronic acids has emerged as one of the most powerful, attractive and convenient synthetic route for the construction of biaryl compounds [1–4]. Although nickel [5] and copper [6] catalysts have also been reported, the palladium appears to be the best catalyst for the C–C coupling reactions due to the high reaction yield and short reaction time [7–9]. In recent years, there has been considerable interest in the preparation of highly active palladium catalysts to facilitate such transformations [10–15]. Most of the palladium catalyzed Suzuki–Miyaura coupling reactions have been performed in organic solvents. However, the use of an environmentally benign reaction medium, minimization of steps, better yields, and faster reaction remained challenges in the context of green chemistry for the Suzuki–Miyaura coupling reaction [16,17]. In this regard, the use of water, the most abundant and non-toxic solvent for organic reactions, is reclaiming its importance due to pressing environmental, economical, and safety concerns [18–22]. Thus far, various catalytic systems have been reported for the Suzuki–Miyaura coupling reaction in water, eventhough the

Suzuki–Miyaura reaction in water may be less efficient than in a suitable organic solvent [23–27]. The palladium catalysts with phosphine ligands [28], carbene ligands [29], resin-supported [30], polymer-supported [31,32], palladacycle [33] and other coordinates [34] have shown high activity in the Suzuki–Miyaura coupling reactions in water. However, problems such as expensive poisonous phosphine ligands and unreusability of the homogeneous catalyst extremely limited the industrial applications. Thus, the development of easily available or readily prepared, inexpensive palladium catalyst with a high activity towards Suzuki–Miyaura cross-coupling reactions in the sole solvent of water is a highly desirable goal.

Transition metal nanoclusters are known to be effective catalysts for chemical reactions due to the high surface-to-volume ratio [35]. However, nanoclusters tend to be fairly unstable in solution and, therefore, special precautions have to be taken to avoid their aggregation or precipitation during the preparation of such nanoclusters in solution [32]. In order to obtain stable nanoclusters dispersed in solution, a stabilizing agent such as polymer is usually added into the reaction system [36,37]. The use of polymeric matrix as stabilizer improves some properties of the nanoclusters such as the solubility, thermal stability and catalytic activity [35]. Palladium nanoparticles stabilized with polymers such as poly(N-vinyl-2-pyrrolidone) [38–40], polystyrene-b-poly(sodium acrylate) [41] and poly(N,N-

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dihexylcarbodiimide) [42] have been used as catalyst in various Suzuki–Miyaura cross-coupling reactions in different solvents, but the reported activities of these catalysts using water as sole solvent are too low for them to be reused for practical organic synthesis. In our recent study, we reported the in situ generation of poly(4-styrenesulfonic acid-co-maleic acid), PSSA-co-MA, stabilized ruthenium(0) and palladium(0) nanoclusters during the hydrolysis of ammonia–borane [43]. The PSSA-co-MA stabilized ruthenium(0) and palladium(0) nanoclusters, in situ generated, show high activity in hydrogen generation from the hydrolysis of ammonia–borane in water. Considering the high activity and dispersibility of PSSA-co-MA stabilized palladium(0) nanoclusters, we extended this study to cover the use of them as catalyst in Suzuki–Miyaura cross-coupling reaction in water as sole solvent without any purification process after the catalytic hydrolysis of ammonia–borane. Herein, we report the further characterizations and the superb catalytic performance of the PSSA-co-MA stabilized palladium(0) nanoclusters in Suzuki–Miyaura cross-coupling reactions of arylboronic acid with various aryl bromides or aryl iodide in aqueous solution under the relatively mild reaction conditions.

2. Experimental

2.1. Materials and methods

Potassium tetrachloropalladate(II) (99%), poly(4-styrenesulfonic acid-co-maleic acid), PSSA-co-MA, and ammonia–borane complex (AB, H_3NBH_3, 97%) were purchased from Aldrich® and used as received. Deionized water was distilled by water purification system (Milli-Q System). All glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with drying in an oven at 150 °C.

2.2. Preparation of PSSA-co-MA stabilized palladium(0) nanoclusters

PSSA-co-MA stabilized palladium(0) nanoclusters were prepared following our reported facile procedure described elsewhere [43]. In a typical procedure, 6.53 mg K_2PdCl_4 (0.02 mmol) and 137.68 mg PSSA-co-MA (0.40 mmol monomer unit) were dissolved in 10 mL water and stirred for 10 min. Next, 63 mg AB (2 mmol) dissolved in 10 mL water was added into the metal–polymer mixture. An abrupt color change from orange to dark brown was observed in less than 15 s indicating the formation of PSSA-co-MA stabilized palladium(0) nanoclusters. Upon completion of the reaction, the as-synthesized nanoparticles were preserved in a Schlenk tube under nitrogen atmosphere to use as catalyst stock solution for Suzuki–Miyaura cross-coupling reactions.

2.3. Characterization of PSSA-co-MA stabilized palladium(0) nanoclusters

The TEM and corresponding selected area electron diffraction (SAED) images were obtained using a JEM-2010 (JEOL) TEM instrument operating at 200 kV. The as-prepared nanoclusters solution prepared as described in Section 2.2 was centrifuged at 8000 rpm for 8 min. The separated nanoclusters were washed with ethanol to remove the excess polymer and other residuals. Then, the nanoclusters sample was redispersed in water. One drop of the colloidal solution was deposited on the silicon oxide coated copper grid and evaporated under vacuum. Samples were examined at magnifications between 60 and 400k. XRD pattern were obtained on a Bruker AXS D8-Advanced diffractometer with Cu Kα radiation (λ = 1.5418 Å).

2.4. Typical procedure for the Suzuki–Miyaura cross coupling reactions

Suzuki–Miyaura coupling reactions were conducted as follows: 3.2 mL aliquot of PSSA-co-MA stabilized palladium(0) nanoclusters (0.01 mmol Pd) taken from the catalyst stock solution (1 mM Pd) was transferred into the Schlenk tube (10 mL) and heated to 100 °C. Then, arylbromide (1.0 mmol), phenylboronic acid (1.5 mmol) and base (2.0 mmol) were added into the Schlenk tube. The progress of the reaction was monitored by gas chromatography (GC) by taking minimum amount of sample from the reaction mixture in certain time intervals. Upon completion of the catalytic reaction, the reaction mixture was cooled and the products extracted with acetone followed by filtration through a pad of silica gel with copious washing, concentration by solvent evaporation and purification by flash chromatography on silica gel. The purity of the compounds was checked by NMR and GC, and conversions are given based on the residual unreacted arylbromides.

2.5. GC analyses

GC analyses were performed on a HP 6890N instrument equipped with a capillary column (5% biphenyl, 95% dimethylsiloxane) (30 m × 0.32 mm i.d. × 0.25 μm film thickness). The GC parameters were as follows: initial temperature, 50 °C; initial time, 1 min; solvent delay, 3.70 min; temperature ramp 1, 10 °C/min; final temperature, 150 °C; temperature ramp 2, 15 °C/min; final temperature, 250 °C; final time, 20.67 min; injector port temperature, 250 °C; detector temperature, 250 °C, injection volume, 2.0 μL.

2.6. Recyclability of PSSA-co-MA stabilized palladium(0) nanoclusters in Suzuki–Miyaura cross-coupling reaction

For a recyclability test, the Suzuki–Miyaura cross-coupling reaction between p-bromobenzene and phenylboronic acid catalyzed by PSSA-co-MA stabilized palladium(0) nanoclusters (0.01 mmol Pd) was performed six times consecutively by adding a new batch of 1 mmol p-bromobenzene and 1.0 mmol phenylboronic acid after each cycle in the presence of Cs_2CO_3 under the same conditions described in the section "Typical procedure for the Suzuki–Miyaura cross coupling reactions". It was assumed that there was no p-bromobenzene remained in the reaction mixture after each catalytic cycle.

3. Results and discussion

PSSA-co-MA stabilized palladium(0) nanoclusters were formed in situ during the hydrolysis of ammonia–borane from the reduction of potassium tetrachloropalladate(II) in aqueous solution according to our facile protocol reported elsewhere [43]. In our previous study, we reported the results on the reduction of potassium tetrachloropalladate(II) in the presence of PSSA-co-MA stabilizer by ammonia–borane in aqueous solution following by UV–vis spectroscopy and the TEM images showing the particle size distribution with an average particle size of 3.5 ± 1.2 nm. Herein, the further characterizations to enlighten the crystalline structure of the PSSA-co-MA stabilized palladium(0) nanoclusters by SAED and XRD are given. Fig. 1 shows the XRD pattern of the PSSA-co-MA stabilized palladium(0) nanoclusters. The observation of three broad peaks at 2θ of 40, 47 and 69 in XRD pattern, readily assigned to the (1 1 1), (2 0 0) and (2 2 0) reflections of fcc-Pd respectively, confirms the crystalline nature of the nanoclusters. The SAED pattern given in the inset of Fig. 2, presenting the electron diffraction of the nanoclusters in the circled area of corresponding TEM image, exhibits three diffused rings indicating (1 1 1), (2 0 0) and (2 2 0) reflections of fcc-Pd, respectively. This is in good agreement with the results obtained
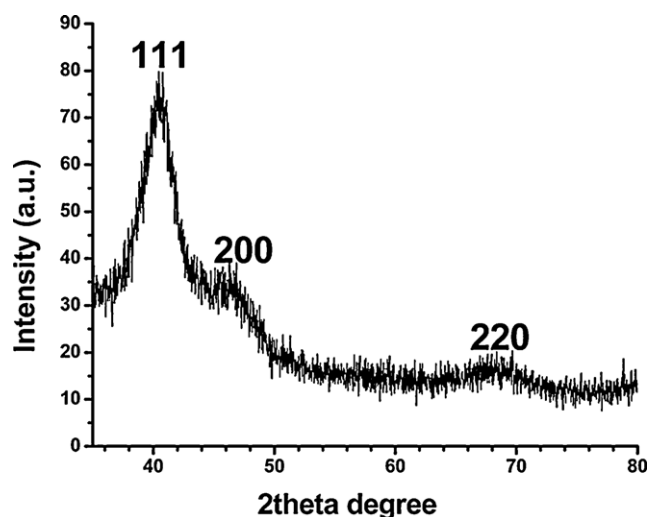
Fig. 1. X-ray diffraction pattern of as-prepared PSSA-co-MA stabilized palladium(0) nanoclusters.

Fig. 2. TEM image and corresponding SAED pattern (inset) of as-prepared PSSA-co-MA stabilized palladium(0) nanoclusters.

by the XRD pattern. Additionally, the particle size of 4.2 nm calculated from the (1 1 1) reflection plane at 2θ of 40 in XRD spectrum by using Scherrer equation is compatible with that of calculated from TEM image (3.5 nm).

The PSSA-co-MA stabilized palladium(0) nanoclusters were used as catalyst in Suzuki–Miyaura cross-coupling reactions in water without any purification after their catalysis in the hydrolysis of ammonia–borane. We used water as sole solvent instead of organic solvent because of the fact that PSSA-co-MA stabilized palladium(0) nanoclusters is highly dispersed in water as determined by TEM images [43]. The results reveal that PSSA-co-MA stabilized palladium(0) nanoclusters are highly active catalyst in Suzuki–Miyaura cross-coupling reactions of various arylboronic acid and aryl bromides or aryl iodide in water at relatively mild reaction conditions. The possible reason for the high activity of the catalyst is the very small particle size as well as the high dispersion of PSSA-co-MA in aqueous solution leading to easy access of substrate to active metal surfaces. In addition to high
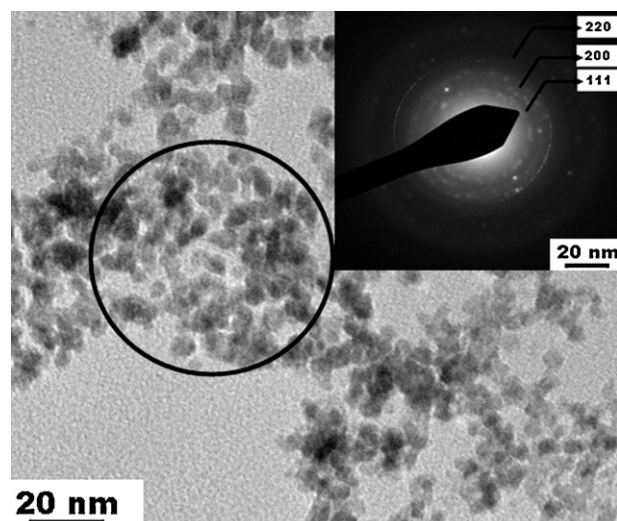
activity, the colloidal PSSA-co-MA stabilized palladium(0) nanoclusters were stable in aqueous solution and no precipitation was observed during the all catalytic reactions. As illustrated in Table 1, initial studies were performed by using different bases (Cs_2CO_3, K_2CO_3 and KO^tBu) and at different temperatures (25, 60, 80 and 100 °C) in order to optimize the reaction conditions for the coupling of p-bromoacetophenone with phenylboronic acid in the presence of PSSA-co-MA stabilized palladium(0) nanoclusters catalyst (0.01 mmol Pd) under aerobic conditions. The reproducibility of each catalytic reaction was confirmed by carrying out the catalytic reaction at least three times. It was found that the best results in terms of yield and reaction time were obtained using KO^tBu as a base at 100 °C in water (Table 1, Entry 15) while no activity was observed at room temperature. A control experiment under the optimized conditions to determine whether the stabilizer (PSSA-co-MA) promotes the Suzuki–Miyaura coupling reaction of p-bromoacetophenone with phenylboronic acid in the

Table 1

Screening of reaction parameters for Suzuki–Miyaura cross-coupling reaction catalyzed by PSSA-co-MA stabilized palladium(0) nanoclusters.
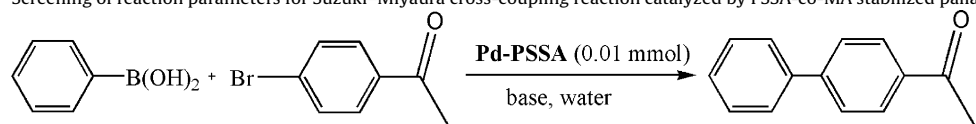
Entry	Base	T (°C)	t (min)	Conv. (%)[a]
1	K_2CO_3	60	60	16
2	K_2CO_3	60	120	85
3	K_2CO_3	60	180	92
4	K_2CO_3	80	30	98
5	K_2CO_3	100	5	82
6	K_2CO_3	100	10	99.5
7	Cs_2CO_3	60	60	36
8	Cs_2CO_3	60	120	96.5
9	Cs_2CO_3	80	30	97
10	Cs_2CO_3	100	10	99.6
11	K^tBuO	60	60	17
12	K^tBuO	60	120	78
13	K^tBuO	60	180	95
14	K^tBuO	80	30	97
15	K^tBuO	100	3	99
16[b]	K_2CO_3	100	15	8.7
17[b]	K_2CO_3	100	30	51.3
18[b]	K_2CO_3	100	60	35.8

[a] *Reaction conditions: p-Bromoacetophenone, 1.0 mmol; phenylboronic acid, 1.5 mmol; water, 3.2 mL; base, 2 mmol; Pd catalyst, 0.01 mmol, open air atmosphere.*

[b] *p-Chloroacetophenone, 1.0 mmol; phenylboronic acid, 1.5 mmol; water, 3.2 mL; base, 2 mmol; Pd catalyst, 0.01 mmol, open air atmosphere.*

Table 2
The Suzuki–Miyaura coupling reactions of aryl bromides with phenylboronic acid catalyzed by PSSA-co-MA stabilized palladium(0) nanoclusters.
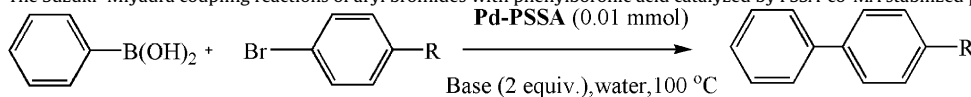
Entry	R	Product	Time (min)	Conv. (%)	TOF (h^{-1})
1	CH$_3$C(O)–		10^a	98	588
			3^b	99	1980
2	CH(O)–		5^a	99	1188
			5^b	97	1164
3	H		5^a	96	1152
			5^b	90	1080
4	H^c		1^a	98	5880
			1^b	99	5940
5	CH$_3$O–		10^a	92	552
			10^b	6	576
6	CH$_3$–		20^a	96	288
			10^b	99	594

Reaction conditions: 1.0 mmol of *p*-R-C$_6$H$_4$Br aryl bromide, 1.5 mmol of phenylboronic acid, 2.0 mmol base, 0.01 mmol (1%) Pd (Cat.), water 3.2 (mL), 100 °C; open air atmosphere.
^{a} Base: Cs$_2$CO$_3$.
^{b} Base: K^{t}BuO.
^{c} Iodobenzene, purity of compounds was checked by NMR and yields are based on arylbromide. All reactions were monitored by GC; TOF = (mol product/mol Cat) × h^{-1}.

absence of palladium indicated that no product was observed within 24 h. Under the optimized reaction conditions, we then evaluated the efficiency of PSSA-co-MA stabilized palladium(0) nanoclusters catalyst for Suzuki–Miyaura coupling reaction of different substrates (*p*-bromoacetophenone, *p*-bromobenzaldehyde, *p*-bromobenzene, *p*-bromoanisole, *p*-bromotoluene and iodobenzene) with phenylboronic acid and the results are summarized in Table 2. It is clearly seen from Table 2 that the Suzuki–Miyaura coupling reaction of phenylboronic acid and iodobenzene or arylbromides bearing either electron donating or electron withdrawing substituents were afforded the corresponding biphenyls in excellent yields with high TOF values without any induction period in the presence of PSSA-co-MA stabilized palladium(0) nanoclusters in water. For example, the coupling reactions of iodobenzene and *p*-bromoacetophenon with phenylboronic acid in the presence of

K^{t}BuO yielding 99% coupling product end up in one and three minutes, respectively (Table 2, Entries 1 and 4). Table 3 shows the various palladium nanoparticle catalyst systems which have been tested in the Suzuki–Miyaura coupling of various arylbromides or iodies with phenylboronic acid to produce the corresponding biaryl compounds in sole water. Compared to catalyst systems given in Table 3, the in situ generated PSSA-co-MA stabilized palladium(0) nanoclusters show superb catalytic activity in coupling of arylbromides with phenylboronic acid under the optimized conditions given in Table 2. It is also noteworthy that the TOF values of 1980 and 5940 h^{-1} (Table 2, Entries 1 and 4) for Suzuki–Miyaura coupling reactions of *p*-bromoacetophenone or iodobenzene with phenylboronic acid catalyzed by PSSA-co-MA stabilized palladium(0) nanoclusters in water, respectively, are one of the highest values ever reported [23]. After obtaining such a high activity

Table 3
Activities of various palladium nanoparticles catalyst in terms of TOF values have been tested for Suzuki–Miyaura cross-coupling of arylbromides or iodides and phenylboronic acid for same amount of reactants in water (1.0 mmol arylbromide and 1.5 mmol phenylboronic acid).
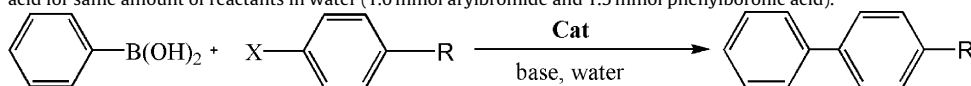
| Entry	R	X	Catalyst	Temp (°C)	Time	Yield (%)	TOF(h^{-1})	Ref.
1	–C(O)CH3	Br	PSSA-co-MA-Pd^0	100	3 min	99	1980	This study
2	–OCH3	Br	PSSA-co-MA-Pd^0	100	10 min	96	576	This study
3	–OCH3	Br	Pd-SDS	100	5 min	95	456	[48]
4	–OCH3	Br	Pd-PEG	25	2 h	98	490	[49]
5	–OCH3	Br	Pd-1/FSG	100	12 h	86	72	[50]
6	–OCH3	Br	Fe$_3$O$_4$-Pd	50	12 h	90	12	[51]
7	–C(O)CH3	Br	Pd-Ps-co-PGMA-IDA	90	4 h	93	24	[52]
8	–OCH3	Br	pEVPBr-Pd	90	9 h	68	38	[53]
9	–C(O)CH3	Br	HAP-Pd^0	100	4 h	94	39	[54]
10	–OCH3	Br	Pd-polystyrene	100	5 h	99	10	[55]
11	–OCH3	I	Pd-CD	100	2 h	95	48	[56]
12	–OCH3	I	Pd-PS-PEO	50	4 h	86	22	[57]
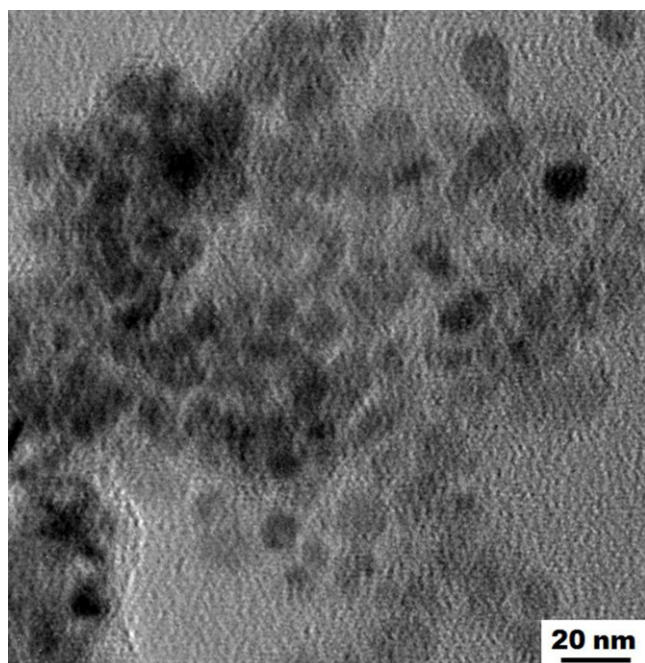
Fig. 3. TEM image of the PSSA-co-MA stabilized palladium(0) nanoclusters after their use as catalyst in the Suzuki–Miyaura coupling reaction in water.

Fig. 4. A recyclability test for PSSA-co-MA stabilized palladium(0) nanoclusters in Suzuki–Miyaura cross-coupling reaction of p-bromobenzene with phenylboronic acid in aqueous solution under optimized reaction conditions.

in Suzuki–Miyaura coupling reactions of p-bromoacetophenone or iodobenzene with phenylboronic acid catalyzed by PSSA-co-MA stabilized palladium(0) nanoclusters in water, we also tried the catalysis of PSSA-co-MA stabilized palladium(0) nanoclusters in the Suzuki–Miyaura coupling reactions of arylchlorides with phenylboronic acid in water. However, the highest conversion was reached up to 51.3% in the presence of K_2CO_3 within 30 min in water at 100 °C (Table 1, Entry 17) and the longer reaction time did not give any further conversion (Table 1, Entry 18). It is well-known that chlorides were generally less reactive towards Suzuki–Miyaura coupling reaction under the same conditions used for the coupling of bromides, iodides, and triflates. The low reactivity of chlorides is usually attributed to the strength of the C–Cl bond (bond dissociation energies for Ph-X: Cl: 96 kcal/mol; Br: 81 kcal/mol; I: 65 kcal/mol) which leads to reluctance by arylchlorides to oxidatively add to palladium(0) centers, a critical initial step in Pd-catalyzed coupling reactions [41,44–47].

Fig. 3 shows the TEM image of the PSSA-co-MA stabilized Pd(0) nanoclusters after their use as catalyst in the Suzuki–Miyaura coupling reactions. The separation of the catalyst from reaction medium was done by centrifugation. The TEM image of the solid sample shows the presence of bigger particles formed compared to original ones, most probably, due to the agglomeration of the particles during the catalysis. The decreasing in the catalytic activity of PSSA-co-MA stabilized Pd(0) nanoclusters in the Suzuki–Miyaura coupling reaction after first catalytic cycle can also be attributed to the agglomeration of the particles during the catalysis. Additionally, the ICP-OES analysis performed on the sample of supernatant solution indicates that there is no etching of palladium into the solution. By considering all of the results obtained for the samples after catalysis, it can be concluded that the PSSA-co-MA stabilized Pd(0) nanoclusters are active species for the catalytic Suzuki–Miyaura coupling reaction in water.

Fig. 4 shows the six runs recyclability test of PSSA-co-MA-stabilized palladium(0) nanoclusters catalyst in the Suzuki–Miyaura cross-coupling of p-bromobenzene with phenylboronic acid performed in the presence of 0.01 mmol PSSA-co-MA-stabilized palladium(0) nanoclusters. PSSA-co-MA-
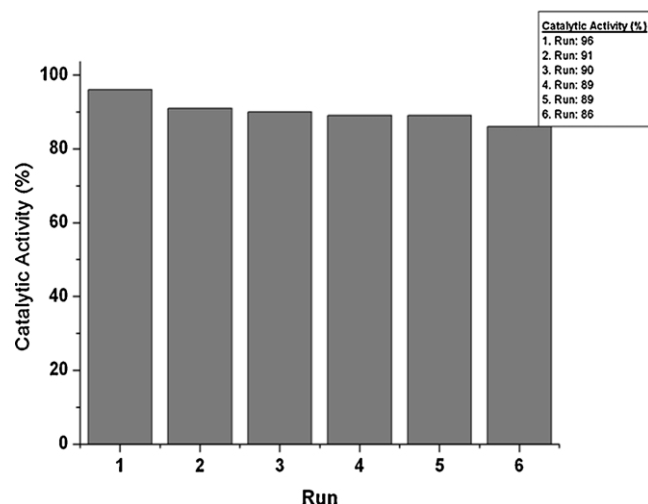
stabilized palladium(0) nanoclusters maintain 86% of their initial catalytic activity at the end of the sixth cycle of Suzuki–Miyaura coupling reaction. This result indicates that PSSA-co-MA stabilized palladium(0) nanoclusters catalysts could be reused in several successive runs without significant loss of initial activity for Suzuki–Miyaura cross-coupling reactions in water.

4. Conclusion

In conclusion, we have shown that the well-defined PSSA-co-MA stabilized palladium(0) nanoclusters can easily be prepared starting with non-toxic commercially available chemicals and serve as efficient, recyclable catalyst for the Suzuki–Miyaura coupling reaction of aromatic bromides and iodides under the relatively mild reaction conditions using water as sole solvent in air. The significant advantages of this protocol are simple operation, very fast reaction time (1 min) and being an environmentally gracious process which can be used to generate a diverse range of biphenyls in excellent yields with the one of the highest TOF values ever reported for the Suzuki–Miyaura coupling reaction catalyzed by palladium nanoparticles catalyst.

Acknowledgements

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