



Preparation of polymer anchored Pd-catalysts: Application in Mizoroki–Heck Reaction

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ABSTRACT

A series of polymer anchored Schiff bases were prepared from chloromethylated styrene–divinylbenzene copolymer beads and loaded with PdCl₂ to get air and water stable supported catalysts. The catalysts were characterized and utilized in Mizoroki–Heck reaction of aryl bromides and iodides.

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1. Introduction

Development of chemical transformations utilizing environmentally compatible and safe methodologies has gained renewed importance. Many efforts are underway to modify the existing important reactions to meet ever increasingly stringent environmental norms. In this effort, immobilization of toxic metal complexes on polymer supports and explore their use in many reactions is of vital consideration [1,2]. The distinct advantage of polymer anchored metal catalysts in conventional reactions is of several folds: simple methods of immobilization, easy recoverability, reusability, effortless extraction, high activity, solvent compatibility, economy when costly metals are used etc. Some of the metals used for catalytic reactions are toxic or undesirable in sensitive products such as pharmaceutical intermediates where the use of heterogeneous catalysts can help to keep the levels of their contamination low and to the acceptable level. The concept of polymer supported metal complexes is widely explored by several researchers and the subject is extensively covered in the recent literature [3–9]. Since the first report by Merrifield on the concept of polymer supported peptide synthesis [10] several significant developments have taken place to use a host of polymeric materials as supports for synthesis and catalysis [11–18]. These include the use of soluble polymer supports [13,14], dendrimers [18,19], polysilox-

ane [20,21], self-supported polymeric catalysts [22], nano-particles [23], metals loaded on clays and zeolites [24,25], metal oxides, mesoporous materials [7], etc.

Polymer prepared by crosslinking of polystyrene and divinylbenzene remains an easily available and well studied support for facile functionalization and hence a support of choice by many groups of researchers. In this paper we report our findings on the synthesis of polymer bound Schiff base ligands, their palladium complexes and applications of the Pd-loaded catalysts for Mizoroki–Heck coupling reaction [26]. There are a few reports on polymer bound phosphine ligands [27–29], but very few of phosphine free N,N type polymer attached Pd complexes have been developed for this reaction [30].

2. Experimental

2.1. Material

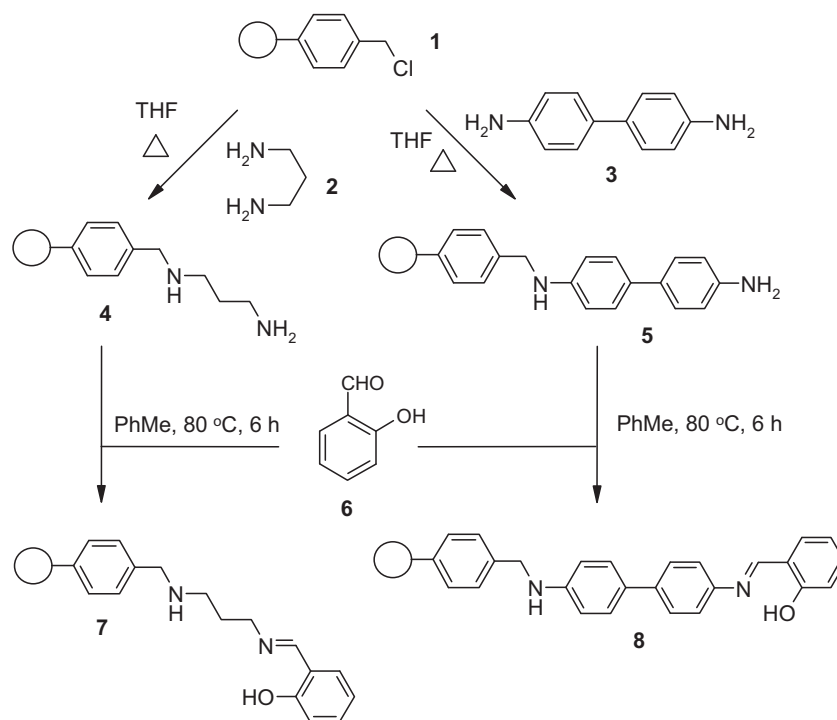
Chloromethylated poly(styrene–divinyl benzene) copolymer spherical beads (0.3–1.2 mm) with 5 or 8% crosslink were supplied by Ion-Exchange (India) Limited, Mumbai. Palladium chloride, 1,3-diaminopropane, 4,4'-diaminobiphenyl and iodobenzene were obtained from Aldrich and used without further purification. Styrene (Fluka) was distilled before use, 4-iodo anisole was prepared from 4-anisidine [31], and other chemicals and solvents of analytical grade were purchased from local suppliers.

2.2. Preparation of polymer anchored chelating ligand

Commercial sample of chloromethylated resin beads were first purified by soxhlet extraction with methanol to remove the sol-

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Scheme 1. Synthesis of polymer anchored Schiff bases.

uble impurities. Purified resin was then stirred for several hours with appropriate quantity of diamines, viz 1,3-diaminopropane **2** and 4,4'-diaminobiphenyl **3** dissolved in tetrahydrofuran such that one of the amino groups is alkylated and other remained free. The beads of product **4** or **5** obtained from the two reactions were separated and washed carefully with the same solvent and then successively with methanol, deionised water, dioxane and again with dry methanol and dried at 50 °C under reduced pressure. Having established the presence of amino group by IR spectral analysis samples of **4** and **5** were heated with excess of salicylaldehyde **6** in toluene at 80 °C [32]. The formation of Schiff base anchored onto the polymer **7** and **8** was established by analytical and IR analysis.

2.3. Loading of Pd(II) on the polymer anchored ligand

The polymer beads of **7** or **8** were kept in ethyl alcohol for one hour in a round bottom flask. These were then treated with 1% (w/v) solution of PdCl₂ in the same solvent, initially at 50 °C for 45 min with occasional shaking and then left on mechanical shaker for 15 days at room temperature. After this time the color of beads changed to brown giving a preliminary indication of loading of the metal on the resin giving polymer anchored Pd-catalyst beads. The beads were separated, washed with ethyl alcohol and dried under reduced pressure at 60–65 °C for 24 h. By this procedure the following polymer anchored Pd-catalysts were prepared: **A-1** and **B-1** with 5% crosslink and **A-2** and **B-2** with 8% crosslink, where **A-1** and **A-2** were obtained from **7** and **B-1** and **B-2** are from **8**.

The present study involves characterization and screening of these four catalysts for the Mizoroki–Heck reaction of aryl halides with styrene to prepare stilbene derivatives.

2.4. Analysis of catalyst

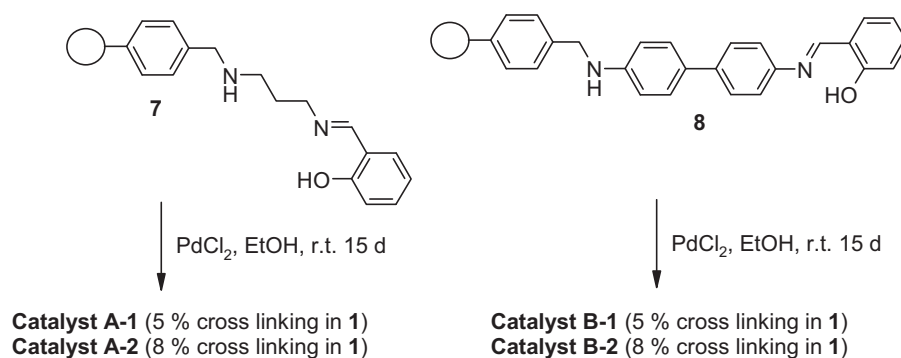
Elemental analysis of the polymer anchored Schiff bases and the corresponding Pd-catalysts were carried out on Coleman Analyzer. The metal contents of the polymer anchored catalysts were

estimated using Perkin-Elmer Atomic Absorption Spectrometer, Model Zeeman ZL-4100, for which a known weight of catalyst was digested with conc. HCl and then diluted to constant volume for the analysis. Surface area of the polymer beads before and after complexation with metal was determined using the BET method with a Carlo-Erba Surface Area Analyzer. The IR spectra in the range of 50–4000 cm⁻¹ were recorded on a Nicolet Manga-550 Spectrophotometer. Thermogravimetric analyses of the catalysts were carried out on Shimadzu DT-30 Analyzer at a heating rate of 10 °C min⁻¹ up to 600 °C under the atmosphere of nitrogen. Diffuse reflectance spectra (200–400 nm) were recorded on a Shimadzu UV-240 instrument using optical grade BaSO₄ as the reference. Scanning electron micrographs of the catalysts and the supports were taken on Jeol JSM-T 300 instrument. Swelling behavior of the freshly prepared catalysts in polar and non-polar solvents and their bulk densities at 27 °C were measured as described previously [33].

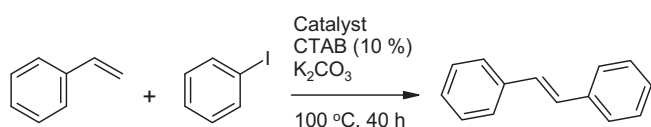
The structures of various stilbenes obtained by catalytic coupling reaction were established by comparing the m.p. with known or reported values and H NMR spectra.

2.5. Procedure for catalytic Heck reaction

The reaction of aryl halide and olefin, usually attached with an electron withdrawing group in presence of Pd-catalyst and a suitable base, Mizoroki–Heck reaction, is an extremely important method of synthesis of substituted stilbene and cinnamic acid derivatives [34–36]. Separation of the used catalysts for further reactions is crucial for viable applications. Also the contamination of palladium in the sensitive products becomes a matter of concern. The variants of catalysts **A** and **B** were taken in solvent and allowed to swell for 30 min, and charged with the reagents for Mizoroki–Heck reaction. Two solvent systems were identified: i. water with small quantity of cetyltrimethylammonium bromide (CTAB) as promoter and ii. dimethylacetamide (DMA) for this reaction, while the third solvent toluene was not very effective. The mixture is heated for several hours and the progress of reaction



Scheme 2. Loading of Pd on polymer supported Schiff bases.



Scheme 3. Standard Mizoroki–Heck reaction.

i.e. formation of stilbene was monitored by thin layer chromatography (see Scheme 3). The products, various substituted stilbenes were separated by column chromatography and their structures were confirmed by comparison of melting point and also from H NMR and mass analysis [37].

2.5.1. Typical procedure for the Mizoroki–Heck reaction

Synthesis of *trans*-4-methoxy-4'-methylstilbene (Table 7, entry-3):

A two neck round bottom flask was charged with 4-iodoanisole (0.1 g; 0.427 mmol), catalyst A-2 (0.091 g; 0.000213 mmol Pd, 0.05 mol%), dry potassium carbonate (0.118 g; 0.855 mmol) and dimethylacetamide (6 mL) under the nitrogen atmosphere. This mixture was slowly heated. As soon as the temperature reaches 65 °C, a solution of 4-methylstyrene (0.076 g; 0.64 mmol) in DMA (2 mL) was introduced. The reaction mixture was then heated to 140 °C and continued for 40 h. The reaction mixture was quenched with water and extracted with ethyl acetate (3 × 25 mL). The combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel to afford *trans*-4-methoxy-4'-methylstilbene (0.09 g, 94.7%) as white solid. m.p. = 164 °C (reported 163–164 °C).

3. Results and discussion

The chemical modification of chloromethylated resin and subsequent loading of palladium is outlined in Schemes 1 and 2. Four different catalysts studied in the present work are designated as:

A-1: 5% poly(S-DVB)Pd(II)(1,3-DAP-SB)

A-2: 8% poly(S-DVB)Pd(II)(1,3-DAP-SB)

Table 1

Physical properties of polymers investigated.

No	Polymer (% crosslink)	Surface area (m ² g ⁻¹)	Moisture content (wt.%)	Bulk density (g cm ⁻¹)	Pore size (cm ³ g ⁻¹)
1	1 (5%)	39.9	–	–	0.20
2	1 (8%)	52.2	–	–	0.21
3	A-1 (5%)	30.5	0.31	0.45	0.12
4	A-2 (8%)	38.2	0.48	0.49	0.15
5	B-1 (5%)	34.6	0.30	0.45	0.10
6	B-2 (8%)	45.4	0.25	0.52	0.13

B-1: 5% poly(S-DVB)Pd(II)(4,4'-DABP-SB)

B-2: 8% poly(S-DVB)Pd(II)(4,4'-DABP-SB)

3.1. Catalyst characterization

The physical properties of supports and catalyst samples were studied and the data is presented in Table 1. The slightly higher surface area observed for **B-2** might be due to relative difference in size of the Schiff base formed from 4,4'-diaminobiphenyl [38].

The elemental analysis data of the supports and the catalysts are presented in Table 2. Substantial decrease in the chlorine content is observed when the Schiff bases **7** and **8** are formed from chloromethylated resin beads **1**. Formation of Schiff base was further confirmed by detection of nitrogen. The loading of palladium in the catalysts was found to be in the range of 1.0–2.5 × 10⁻⁴ g/g of resin.

The choice of suitable solvent for catalytic reactions is very crucial for maximizing the activity of supported catalysts. Better swelling behavior results in easier access of the reagents to the active sites to undergo efficient catalytic cycle of the required conversion. It is seen that polar solvents are generally better swelling agents than aliphatic or aromatic non-polar solvents (Table 3). Interestingly, water exhibited maximum degree of swelling. In fact, the present study of Mizoroki–Heck reaction needs polar solvents. The swelling behavior of the catalysts showed water and dimethylacetamide (DMA) to be suitable.

Thermogravimetric analysis of the supported Pd-catalysts reveal that they are quite stable up to 300–325 °C (Table 4), but for a small initial weight loss which might be due to traces of moisture. The weight loss above 300 °C may be due to the dissociation of anchored ligand and/or breaking of polymeric chain. The present analysis shows that the catalysts can be safely used in any standard Mizoroki–Heck reaction where the reaction temperature is maintained around 140 °C.

Although the scanning electron micrographs are featureless, they do exhibit change in morphology while going stepwise from chloromethylated beads to the final polymer anchored catalysts.

The UV–vis reflectance spectra of the synthesized catalysts in BaSO₄ matrix exhibit weak intensity absorption bands in the region

Table 2Elemental analyses of chloromethylated polymer **1**, their Schiff bases **7** and **8** and supported Pd(II) catalysts. All **a** for 5% crosslink, **b** for 8% crosslink.

No	Sample	% C	% H	% Cl	% N	Pd (g/g of resin)
1	1a (with 5% crosslink)	74.2	6.0	15.6	–	–
2	1b (with 8% crosslink)	72.8	6.0	27.6	–	–
3	7a (with 5% crosslink)	81.6	7.3	10.9	4.9	–
4	7b (with 8% crosslink)	78.1	6.2	13.4	4.7	–
5	8a (with 5% crosslink)	80.1	7.0	9.7	4.9	–
6	8b (with 8% crosslink)	75.6	6.1	13.9	2.4	–
7	A-1	71.9	7.1	–	4.0	1.0×10^{-4}
8	A-2	72.1	6.0	–	3.2	2.5×10^{-4}
9	B-1	72.0	6.9	–	3.0	2.0×10^{-4}
10	B-2	70.8	6.3	–	2.3	1.7×10^{-4}

Table 3

Swelling data of supported catalysts (mol%).

No	Solvent	A-1	A-2	B-1	B-2
1	Water	6.67	6.15	6.79	6.26
2	Methanol	5.06	4.45	5.39	4.32
3	Ethanol	4.06	3.72	3.41	5.02
4	Acetonitrile	3.73	3.36	3.12	3.43
5	Dichloromethane	3.80	3.40	3.01	3.10
6	Dioxane	2.99	3.15	2.66	3.02
7	DMF	3.12	2.60	2.46	2.74
8	Acetone	2.84	3.15	2.36	2.68
9	THF	1.94	2.18	1.90	1.63
10	Toluene	1.59	1.79	1.65	1.41
11	Cyclohexane	2.68	1.80	1.59	1.41
12	n-Heptane	0.82	1.31	1.51	0.84

Table 4

Thermogravimetric data of support and palladium anchored catalysts.

No	Sample	Degradation temp. (°C)	Wt. loss (%)
1	1a (5% crosslink)	478	33.0
2	1b (8% crosslink)	469	31.0
3	A-1	380	16.8
4	A-2	348	15.2
5	B-1	397	22.6
6	B-2	350	12.0

330 nm for palladium supported catalysts, which are assigned to the d–d transition of the metal. Ligand to metal charge transfer bands (LMCT) are not seen in this region.

The mid IR (4000–400 cm⁻¹) and far IR (500–50 cm⁻¹) spectra of polymer supported palladium complexes at different stages of the synthesis were studied to elaborate on the nature of coordination of the metal ion to the polymer. The peaks in the region of 3449–3407 cm⁻¹ is due to $\nu_{(N-H)}$ stretching frequency, which show slight shift to lower wave number due to the coordination. Medium intensity band at 1639–1633 cm⁻¹ corresponding to $\nu_{(C=N)}$ (azomethine) in polymer anchored Schiff base is shifted to lower wave numbers (1606–1600 cm⁻¹) on complexation with palladium indicating “N” coordination of the ligand to the Pd(II) metal ion. The spectra also shows a weak intensity bands at 490–450 cm⁻¹ for $\nu_{(Pd-N)}$, around 300 cm⁻¹ for $\nu_{(Pd-Cl)}$ and 380–320 cm⁻¹ for $\nu_{(Pd-O)}$

Table 5IR spectral data of **7**, **8** and metal complexes.

Sample	$\nu_{(N-H)}$ (cm ⁻¹)	$\nu_{(C=N)}$ (cm ⁻¹)	$\nu_{(Pd-O)}$ (cm ⁻¹)	$\nu_{(Pd-N)}$ (cm ⁻¹)	$\nu_{(Pd-Cl)}$ (cm ⁻¹)
7a (5% crosslink)	3449 _{br}	1633 _s			
7b (8% crosslink)	3432 _{br}	1639 _s			
8a (5% crosslink)	3407 _{br}	1634 _s			
8b (8% crosslink)	3409 _{br}	1638 _s			
A-1	3436 _{br}	1633 _s	320	485	302
A-2	3409 _{br}	1606 _s	354	479	303
B-1	3429 _{br}	1633 _s	350	462	302
B-2	3430 _{br}	1600 _s	375	456	302

indicating the coordination of metal with ligand to form the complex on polymer support (Table 5).

3.2. Catalytic Heck reaction

The main goal to support metal complex on polymer matrix is to enhance the life of resulting catalyst, ensure easy separation of it from reaction products, make it feasible to reuse the catalyst and hence increase its overall efficacy. This requires necessary modification of the surface of polymer in order to easily complex metal ions on it. One effective way to do this is by attaching a chelate of appropriate Schiff base to a suitable organic polymer [39–44] or modified silica [45], chitosan [46] and zeolite [47]. In the present study chloromethylated styrene–divinyl benzene copolymer is attached with a Schiff base with two kinds of linker groups CH₂–CH₂–CH₂ in series-**A** and C₆H₄–C₆H₄ in series-**B**. The size and shape of linker group is one variation being studied in order to be able to fine tune the solid catalyst for particular application.

The polymer anchored Pd-catalysts were screened for the standard reaction of synthesis of stilbene by reaction of iodobenzene and styrene in presence of base (Scheme 3). The results are presented in Table 6.

All the four catalysts prepared were quite effective and the products were obtained in good yield with respectable TON for the reactions. Catalyst **A-2** was slightly more active since its crosslink and loading is also higher. The reaction was carried out in water at 100 °C with a small quantity of CTAB to increase solubility of reagents. While toluene gave poor yield probably due to the poor swelling of beads and hence ineffective penetration of reagents to reach the active sites, the other solvents, DMA and DMF are found to be active for this reaction.

Having established that the catalyst **A-2** and **B-1** are more effective among catalysts studied, number of different aryl iodides and aryl bromides were screened with styrene and its derivatives to see the generality of the system. The results are summarized in Table 7. For this study a slightly higher quantity of the catalyst is taken (0.05 mol% of Pd) and a combination of water and DMA is used. The choice of solvent is based on the solubility of aryl halides and styrene. From the point of view of environmental safety it is beneficial to explore the possibility to use water as solvent, prefer-

Table 6
Screening of supported catalysts for standard Mizoroki–Heck reaction.^a


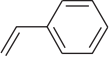
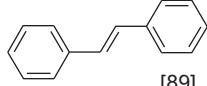
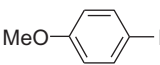
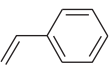
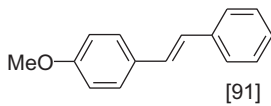
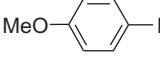
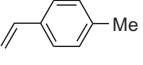
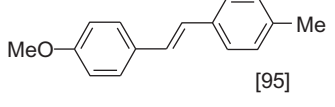

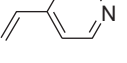
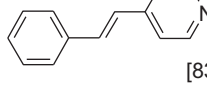
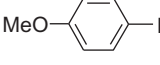
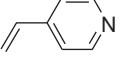
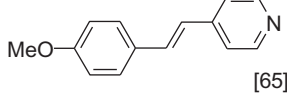

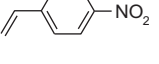
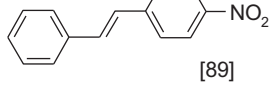

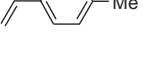
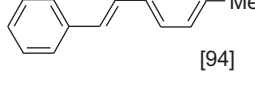




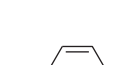
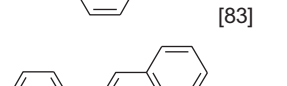

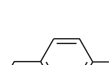
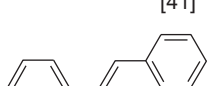

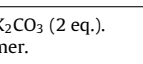

No	Catalyst	Pd content ^b (g/g resin)	Crosslink (%)	Yield ^c (%)	TON
1	A-1	1.0×10^{-4}	5	73	7301
2	A-2	2.5×10^{-4}	8	96	9580
3	B-1	2.0×10^{-4}	5	93	9294
4	B-2	1.7×10^{-4}	8	89	8897

^a All reactions were run for 40 h at 100 °C with CTAB (10 mol%).

^b Pd content (0.01 mol%) for all reactions.

^c Isolated product, pure *trans* isomer.

Table 7
Application of the catalyst for palladium catalyzed Mizoroki–Heck reaction.^a

No.	ArX	Olefin	Solvent {ratio} [Temp. °C]	Catalyst A-2 [mol% of Pd]	Stilbene [yield/%] ^b	TON
1			DMA [140]	[0.001]	 [89]	88,408
2			H ₂ O ^c [100]	[0.01]	 [91]	9089
3			DMA [140]	[0.05]	 [95]	1886
4			DMA–H ₂ O {2:1} [120]	[0.05]	 [83]	1675
5			DMA–H ₂ O {2:1} [120]	[0.05]	 [65]	1290
6			DMA [140]	[0.05]	 [89]	1784
7			DMA [140]	[0.05]	 [94]	1878
8			DMA [140]	[0.05]	 [85]	1700
9			DMA [140]	[0.05]	 [83]	1660
10			DMA [140]	[0.05]	 [41]	812
11			DMA [140]	[0.05] ^d	 [50]	1004

^a All reactions run for 40 h with K₂CO₃ (2 eq.).

^b Isolated yield, mostly *trans* isomer.

^c With CTAB (10%).

^d With **B-1**.

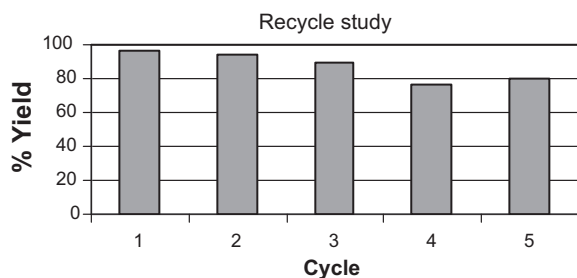


Fig. 1. Recycle study of the catalyst **A-2** for standard reaction of iodobenzene and styrene.

ably singly or as combination with some polar organic solvent. In all the reactions it is very important to stir the contents continuously but carefully using a small spherical shaped magnetic stirrer bar in order to keep the beads in good shape.

The Mizoroki–Heck reaction involves three main steps in the catalytic cycle, viz oxidative addition of aryl halide to Pd, insertion of styrene and finally reductive elimination of stilbene [34–36]. As expected the addition of aryl bromide was less effective due to stronger Ar–Br bond than the corresponding iodides, hence lower yields were observed for them. Under the present catalytic condition aryl chlorides were almost completely ineffective for the olefination reaction.

3.3. Catalyst recycle study

The ease of separation and reuse of the polymer anchored Pd-catalyst are important. The catalyst beads were separated carefully from first cycle where water was used as solvent with CTAB (10%) and washed several times with water, then with methanol and dried under vacuum. The recovered catalyst when reused for identical reaction showed only marginal drop in the conversion (see Fig. 1) in next two cycles. However, there was noticeable drop in the yield in the fourth cycle and the beads started to get coated with white material – most likely polystyrene, formed by the polymerization of styrene. However, the catalyst beads from the fourth cycle when subjected to additional cleaning with toluene before reuse in the fifth cycle showed some recovery in activity, confirming the possibility of polystyrene being deposited and blocking the access of reagents to catalytic sites in the earlier cycle.

4. Conclusion

Chloromethylated poly(styrene–DVB) supported Schiff base palladium(II) complexes **A-1**, **A-2**, **B-1** and **B-2** were prepared and characterized. These supported complexes were found to be very effective catalysts for Mizoroki–Heck reaction for aryl iodides and aryl bromides with number of styrenes. The catalysts could be easily recycled and effectively reused after simple washing.

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