Diethanol Amine-Functionalized Polymer-Supported Palladium (0) Complex as Catalyst for Suzuki Cross-Coupling Reaction in Water

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ABSTRACT: Diethanol amine-functionalized polymer-supported palladium (0) complex as catalyst for Suzuki cross-coupling reaction in water was synthesized and characterized. The catalyst exhibits excellent catalytic activity and stability in the Suzuki cross-coupling reaction. Various aryl bromides were coupled with aryl boronic acids in water, under air, and in the presence of 0.5 mol % of the catalyst to afford corresponding cross-coupled products in high yields at 100°C. Furthermore, the heterogeneous catalyst can be readily recovered by simple filtration and reused for several times only with a slight decrease in its activity. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 286–291, 2011

Key words: functionalized polymer; palladium (0) complex; Suzuki cross-coupling; water

INTRODUCTION

Palladium as catalyst has played a significant role in organic synthesis over the past two decades.[1] Palladium-catalyzed coupling reactions such as Heck reaction,[2–5] Suzuki reaction,[6–8] Stille reaction,[9–11] Trost–Tsuji reaction,[12–14] and Sonogashira-coupling[15,16] have become more and more powerful attractive methods for the formation of carbon–carbon bonds. Various palladium catalysts in homogeneous systems for the Suzuki coupling reaction have been investigated up to date.[17] Although homogeneous palladium catalysts have proven to be efficient, it is difficult to recover them from the reaction system, and using homogeneous palladium catalysts is still uneconomic for industrial applications. So, the development of efficient and recoverable palladium catalysts has received much more attention in recent years.

Heterogeneous palladium catalysts have been widely investigated because such kind of catalysts not only show excellent catalytic activities, but also can be easily recovered and reused.[18–20] Different supports have been reported for immobilization of palladium catalysts recently, including sepiolites,[21,22] hydrotalcite,[23] silica,[24] fluorous silica gel,[25,26] zeolite,[27–29] carbon,[30] and so on.[31] A few palladium complexes supported on functionalized polymer have been reported in some reactions successfully. Li et al.[32] have reported the use of polymer-supported 1,4-diazabicyclo[2.2.2]octane palladium complex for the Suzuki cross-coupling reaction successfully. The polymer-supported salen-type complex as a catalyst has also been used to catalyze Suzuki reaction.[33] However, most of them are still subjected to the use of organic solvent.

Water as solvent in transition-metal catalysis is expected to contribute to its utilization for the development of benign chemical process and products.[34] The development of heterogeneous catalysis in water seems particularly suitable for the Suzuki cross-coupling reaction because of the excellent stability of boronic acids in aqueous media.[35–37] Gallon et al.[38] reported the preparation of biphenyls by the palladium nanoparticles supported on polyaniline nanofibers-catalyzed Suzuki reaction of chloroarenes and boronic acids. Ligandless Pd/C catalyst has showed high activity for the Suzuki cross-coupling reaction in water, and the catalyst could be reused for several times.[39,40] An amphiphilic polymer-supported *N*-heterocyclic carbene palladium complex has also been described for Suzuki reaction in water.[41] As a part of our program aimed at designing new functional supported catalysts and in continuation of our interest in green chemistry, herein we reported a new functionalized polymer-supported palladium (0) complex and its application in the Suzuki cross-coupling reaction in water.

EXPERIMENTAL

Materials and equipments

Chloroacetylated polystyrene (7% divinylbenzene, 15.4% chlorine, grain size range: 240–280 μm, surface
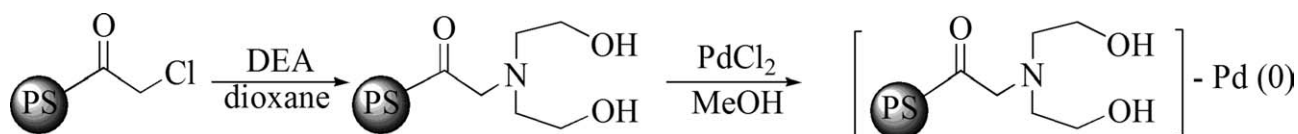
Scheme 1 Preparation of the functional polymer and its corresponding palladium complex.

area: 32 m^2 g^{-1}, pore diameter: 80–100 Å, total pore volume: 0.11 cm^3 g^{-1}) was obtained from Nanjing Microspheres Co. (Nanjing, China). Diethanol amine (DEA), palladium chloride, and other chemicals were obtained from commercial sources and used without further purification. Infrared (IR) spectra were recorded in KBr disks with a Shimadzu IRPrestige-21 Fourier transform-IR spectrometer. Elemental analyses were performed on an Elementar (Germany) Vario ELIII recorder. ^{1}H-nuclear magnetic resonance spectra were measured with a Bruker Avance RX300 analyzer. Gas chromatography-mass spectrometry (GC-MS) analyses were performed on a Saturn 2000GC/MS instrument. Palladium content of the catalyst was measured by inductively coupled plasma on VISTA-MPX analyzer. X-ray photoelectron spectroscopy (XPS) analysis was performed with the PHI-5702/ESCA/SAM equipped with an Mg Kα (1253.6 eV) X-ray source.

Preparation of functional polymer support

DEA-functionalized polymer was synthesized according to the literature method.[42] Prewashed chloroacetylated styrene-divinylbenzene copolymer beads (1.0 g, 4.3 mmol of Cl) were swollen in 30 mL of dioxane for 2 hr. DEA (1.05 g, 10 mmol) was added, and the mixture was stirred at 110°C for 24 hr in the presence of pyridine (0.79 g, 10 mmol). The color of the beads changed from brown to yellow, indicating the attachment of DEA. The beads were then filtered off, washed with water and methanol, and dried at 80°C under vacuum overnight to afford 1.316 g of functional beads. The DEA content of the functional beads was 3.5 mmol g^{-1} according to the result of elemental analyses.

Preparation of polymer-supported palladium (0) complex

The functionalized polymer beads (0.18 g) were swollen in MeOH (10 mL) for 1 hr. To this was added a methanolic solution (10 mL) of PdCl$_2$ (0.065 g, 0.37 mmol), and the mixture was refluxed for about 24 hr. The color of the beads changed from yellow to black, indicating the attachment of palladium nanoparticles. The resulting beads were filtrated, washed with water and methanol, and then dried *in vacuo* at 100°C overnight. The content of

palladium was 1.41 mmol/g as determined by inductively coupled plasma.

General procedure for Suzuki cross-coupling reaction and recycling of catalyst

Under air atmosphere, a round-bottomed flask was charged with aryl halide (2.0 mmol), phenylboronic acid (3.0 mmol), K$_3$PO$_4$ (4.0 mmol), water (6 mL), and catalyst (0.007 g, 0.5 mol%). The mixture was refluxed at 100°C for a certain time (monitored by GC). After cooling to room temperature, 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 the filtrate was separated, dried over Na$_2$SO$_4$, and evaporated. The yields were determined by GC using *n*-dodecane as an internal standard. The crude products obtained were purified by flash chromatography with *n*-hexane/EtOAc as the eluent, affording the corresponding product.

RESULTS AND DISCUSSION

Characterization of the functional polymer and its corresponding palladium (0) complex

The supported catalyst was readily prepared in two steps from chloroacetylated polystyrene. Treatment of the polymer with DEA provided the corresponding functional support, which was then treated with palladium chloride in MeOH to yield of the catalyst as dark beads (Scheme 1).

To ascertain the attachment of DEA and palladium onto the polymer support, IR spectra were recorded separately at different stages of preparation. It can be seen from Figure 1, the C—Cl peaks at 1286 and 702 cm^{-1} in the raw polymer disappeared or weakened after the introduction of DEA. Instead, a strong and broad band at 3400 cm^{-1} in curve B and curve C were assigned to the —OH vibration, and the sharp peaks at 1100–1250 cm^{-1} were attributed to the C—N vibration. Moreover, sharp peaks at about 1650–1750 cm^{-1} in the three curves were attributed to the vibration of C=O.

Furthermore, obvious differences were found when comparing curve B and curve C. It revealed that the peak of C=O vibration had shifted to lower wavenumbers from 1713 to 1701 cm^{-1}, suggesting the coordination of C=O and Pd. There was also a shift toward lower wavenumbers of the C—N
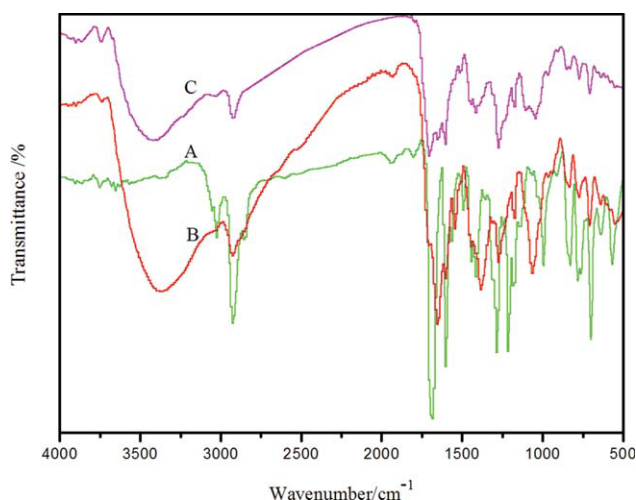
Figure 1 IR spectra of chloroacetylated resin (A), DEA-functionalized resin (B), and support catalyst (C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

absorption peaks from 1068 to 1041 cm^{-1}, indicating the coordination of N and Pd. It was difficult to tell whether the peak of —OH changed after introducing Pd because the broad peak. However, the peak of the C—O vibration had shifted to higher wavenumbers from 1264 to 1277 cm^{-1}.

XPS analysis of functional polymer and supported catalyst was also performed to confirm the formation of the complex. As shown in Table I, the $Pd_{3d5/2}$ binding energy of the metal complex was decreased by 1.5 eV compared with $PdCl_2$. The change of $Pd_{3d5/2}$ binding energy reflects an increase in its electron density. The N_{1s} binding energy of the ligand and complex was 399.1 and 400.0 eV, respectively, which means that there is a coordination effect between nitrogen and palladium. XPS analysis of the oxygen atoms of the complex showed two peaks, which attributed to C=O and —OH. The binding energy of $O1_{1s}$ of the complex was increased by 0.2 eV and $O2_{1s}$ was increased by 0.3 eV compared with those of the ligand, indicating that the there is coordination effect between C=O and Pd, also —OH and Pd. All these results indicated that the polymer-supported palladium (0) complex was formed.

The morphology of the supported catalyst was studied by transmission electron microscopy. Trans-

TABLE I
XPS Data of $PdCl_2$, DEA Functional Resin, and the Support Catalyst[a]

Sample	$Pd_{3d5/2}$	N_{1s}	$O1_{1s}$	$O2_{1s}$
Catalyst	336.8	400.0	533.5	532.1
Functional polymer	–	399.1	533.3	531.8
$PdCl_2$	338.3	–	–	–

[a] The binding energies are referenced to C_{1s} (284.6 eV).
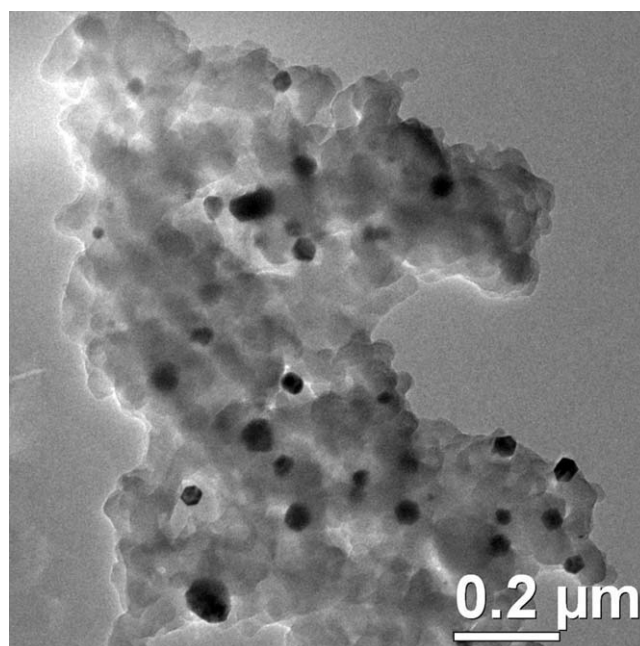
Figure 2 Transmission electron microscopy image of the diethanol amine-functionalized polymer-supported palladium (0) complex.

mission electron microscopy images showed the presence of palladium nanoparticles of about 20 nm size distributed on the surface of the polymer matrix (Figure 2).

Optimization of corresponding reaction conditions

To check the potency of DEA-functionalized polymer-supported palladium (0) complex, it was used in Suzuki coupling reaction, which is a versatile and
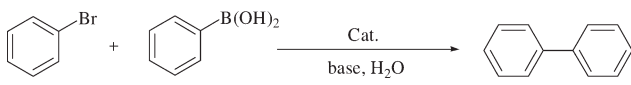
TABLE II
Effect of Solvent on Suzuki Reaction between Bromobenzene and Phenylboronic Acid[a]

Entry	Solvent	Temperature (°C)	Time (hr)	Yield (%)[b]
1	DMF	100	4	97
2	EtOH	78	4	96
3	CH_3CN	81	5	64
4	Toluene	110	4	35
5	MeOH	66	4	80
6	THF	66	6	48
7	H_2O : EtOH (1 : 1)	80	4	97
8	H_2O	100	4	99

[a] Reaction conditions: bromobenzene (2.0 mmol), phenylboronic acid (3.0 mmol), K_2CO_3 (4.0 mmol), Cat. (0.5 mol%), solvent (6 mL).
[b] Isolated yield.

TABLE III
Optimization of the Reaction Conditions[a]

Entry	Catalyst loading (mol %)	Base	Time (hr)	Yield (%)[b]
1	0.5	K_3PO_4	4	99
2	0.5	K_2CO_3	4	92
3	0.5	Na_2CO_3	4	88
4	0.5	NEt_3	6	50
5	0.5	KF	5	61
6	0.5	NaOAc	4	73
7	0.1	K_3PO_4	4	78
8	0.01	K_3PO_4	8	20

[a] Reaction conditions: bromobenzene (2.0 mmol), phenylboronic acid (3.0 mmol), base (4.0 mmol), Cat. (0.5 mol%), H_2O (6 mL), 100°C.
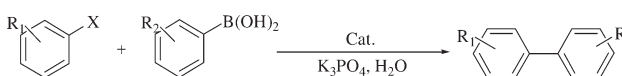[b] Isolated yield.

most studied method for generation of C-C bond in organic synthesis. To optimize the reaction conditions, the coupling between bromobenzene and phenylboronic acid was chosen as model reaction, and various parameters, including solvents, bases, and catalyst loadings were investigated. Among the commonly used solvents, H_2O was the most productive

solvent (Table II, Entry 8). Slightly lower yields were obtained when dimethylformamide, EtOH, and EtOH/H_2O were used as the solvent (Table II, Entries 1, 2, and 7). However, the lower activity of the catalyst was found in other solvents such as CH_3CN, toluene, MeOH, and tetrahydrofuran (Table II, Entries 3–6).

Base also plays a significant role in the rate and the product distribution of the Suzuki cross-coupling reaction. Then, different kinds of bases such as K_2CO_3, Na_2CO_3, NaOAc, KF, and K_3PO_4 for the coupling reaction were investigated (Table III). As can be seen in Table III, K_3PO_4 was found to be the most effective base (Table III, Entry 1). Also, the organic base NEt_3 was studied, but not satisfactory yield was obtained (Table III, Entry 4). Besides, different catalyst loadings were also tested for the reaction. However, only moderate and low yields were obtained when 0.1 mol % and 0.01 mol % of catalyst was used for the reaction, respectively, (Table III, Entries 7 and 8). Thus, we selected K_3PO_4 as the base, H_2O as the solvent, and 0.5 mol % of catalyst, which are the best conditions for the Suzuki cross-coupling reaction.

Under the optimized conditions obtained, we examined the scope for this coupling reaction in water. As shown in Table IV, a wide range of functional groups has also been tolerated in the reaction. The electron-withdrawing groups and electron-donating groups in aryl halides have relatively little effect

TABLE IV
Suzuki Cross-Coupling of Aryl Halides with Arylboronic Acids[a]

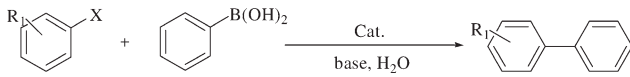| Entry	X	R_1	R_2	Additive	Time (hr)	Yield (%)[b]
1	Br	H	H	–	4	99(97,98,95,93,90,87)[c]
2	Br	p-NO_2	H	–	3	99
3	Br	p-CH_3	H	–	4	96
4	Br	p-CH_3O	H	–	4	94
5	Br	p-CF_3	H	–	3	98
6	Br	p-CH_3CO	H	–	4	96
7	Br	p-CHO	H	–	4	97
8	Br	o-CH_3	H	–	5	90
9	Br	H	p-CH_3	–	4	91
10	Br	H	p-CH_3O	–	4	93
11	Br	H	p-Cl	–	5	85
12	Cl	p-CH_3	H	–	7	6(44)[d]
13	Cl	p-NO_2	H	–	7	11(31)[d]
14	Cl	p-NO_2	H	TBAB	7	92(90,87,83,76)[c]
15	Cl	p-CH_3O	H	TBAB	7	14(39)[d]
16	Cl	p-CH_3	H	TBAB	7	16(21)[d]

[a] Reaction conditions: bromobenzene (2.0 mmol), phenylboronic acid (3.0 mmol), K_3PO_4 (4.0 mmol), Cat. (0.5 mol%), TBAB (1 mmol), H_2O (6 mL), 100°C.
[b] Isolated yield.
[c] Catalyst was reused.
[d] Yield for homo-coupling product of phenylboronic acid.

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TABLE V
Activities of Various Palladium (0) Nanoparticles Catalyst Have Been Tested for
Suzuki Cross-Coupling of Arylhalides and Phenylboronic Acid

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Entry	R	X	Cat. (mmol)	Temperature (°C)	Time (hr)	Yield (%)	Ref.
1	4-C(O)CH$_3$	Cl	Pd-PANI	100	2	91	38
2	4-OCH$_3$	Br	Fe$_3$O$_4$-Pd (0.07)	50	12	90	43
3	4-C(O)CH$_3$	Br	HAP-Pd (0.006)	100	4	94	44
4	4-OCH$_3$	Br	Pd-1/FSG (0.001)	100	12	86	25
5	4-OCH$_3$	I	Pd-PS-PEO (0.01)	50	4	86	45
6	4-OCH$_3$	I	Pd-CD (0.01)	100	2	95	46
7	4-OCH$_3$	Br	Cat. (0.005)	100	4	94	This study

on the coupling reaction. However, aryl chlorides were not active for the reaction, and homo-coupling products of phenylboronic acid obtained even prolonged the reaction time (Table IV, Entries 12 and 13). It is worth to note that the cross-coupling reaction with aryl chlorides could proceed smoothly when tetra-*n*-butyl ammonium bromide was added but only toward the aryl chloride bearing strong electron-withdrawing substituents (Table IV, Entry 14). In addition, recycling studies were also investigated, which showed that the catalyst could be recovered by simple filtration and reused for several times with slight loss in its activity (Table IV, Entries 1 and 14).

As a comparison, Table V shows the various palladium nanoparticle catalyst systems, which have been tested in the Suzuki coupling of various aryl halides with phenylboronic acid to produce the corresponding biaryl compounds in water. Compared with catalyst systems given in Table V, it is worth to note that DEA-functionalized polymer-supported Pd (0) complex showed excellent catalytic activity for coupling of arylbromides with phenylboronic acid under the conditions given in Table IV.

Furthermore, hot filtration experiment was performed to determine whether the reaction proceeded in a heterogeneous or a homogeneous situation.[47] We focused on the coupling reaction of bromobenzene and phenylboronic acid. The reaction was stopped after 20 min, a solid catalyst was separated as described above, and the resulted solution was heated for 6 hr. However, we found that, after this hot filtration, no further reaction was observed. These results strongly indicated that the reaction proceeded over the catalyst surface with a heterogeneous fashion.

CONCLUSIONS

In summary, we have developed a simple and efficient polymer-supported palladium (0) complex for the Suzuki cross-coupling reaction in water. The catalyst has showed highly catalytic activities for the reactions, affording a diverse range of biphenyls in excellent yields within 3 ~ 5 hr. The catalyst could be easily recovered by simple filtration and could be reused for six times without significant loss in its activity. Moreover, the combination of the heterogeneous catalysis system and the use of water as solvent are expected to contribute to its use for the development of benign chemical process and products.

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