



Chitosan-g-mPEG-supported palladium (0) catalyst for Suzuki cross-coupling reaction in water

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ABSTRACT

A chitosan-g-mTEG (methoxy triethylene glycol)- or mPEG (methoxy polyethylene glycol)-supported palladium (0) catalyst was prepared for the Suzuki cross-coupling reaction in water. The catalyst showed excellent catalytic activity in the Suzuki cross-coupling reaction without additional phase transfer reagents due to the enhanced solubility of the organic substrate by PEG grafting. In addition, the catalyst could be reused up to five times with the catalytic activity being recovered easily after simple manipulations.

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1. Introduction

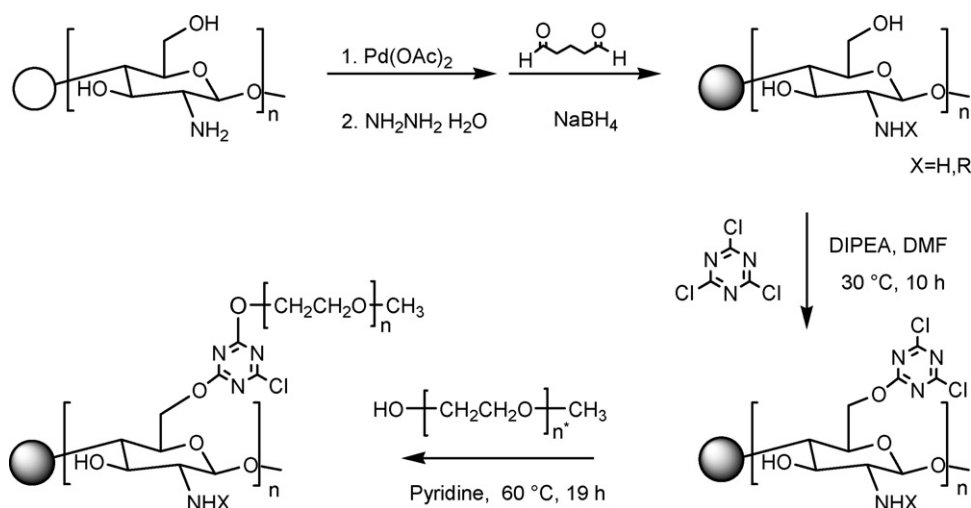
The palladium catalyzed Suzuki cross-coupling reaction is one of the most powerful tools for the formation of carbon–carbon bond in organic synthesis especially as this pertains to biaryl compounds [1–3]. Thus far, a considerable number of homogenous palladium catalysts have been used to obtain high yields of desired product. However, separation of the catalyst and ligands from the final product is the problem to be solved. In this regard, studies on heterogeneous catalysts have drawn much attention because they can be easily separated and recovered [4–6] despite the fact that their catalytic activity is lower than that of homogeneous catalysts. Recently, numerous solid-supported palladium catalysts have been reported that utilize mild and/or environmentally benign reaction conditions. These supported catalysts were prepared by immobilizing palladium (II) on supported ligands [7–19] (phosphine, amines, *N*-heterocyclic carbene) or ligand-free palladium (0) nanoparticles on various solid supports (polystyrene [20], silica [21], cellulose [22], corn starch [23], polymethyl methacrylate [24] and others [25]).

Nowadays, “Green Chemistry” has attracted considerable attention particularly in organic synthesis due to its economic and environmental aspects [26,27]. An increasing number of studies have focused on a variety of supports for the immobilization or

incarceration of palladium (0) nanoparticles with the aim of showing biodegradability, water-miscibility and the metal ion uptake ability for palladium catalyzed cross-coupling reactions. Chitosan, the second most abundant biopolymer in nature next to cellulose, is an ideal polymer support for the immobilization of metal catalysts on account of its high efficiency for metal ion uptake, biocompatibility, chemical and physical versatility [28–32]. Recently, several groups have reported the use of chitosan as a polymer support for palladium catalyzed carbon–carbon coupling reaction. Hardy et al. reported chitosan-2-pyridinecarboxaldehyde complex-supported palladium catalysts for Suzuki and Heck reactions [30]. Cui et al. used a modified chitosan complex-supported palladium catalysts for the Heck reaction [31]. However, the palladium loading amount was relatively low and an organic solvent was used for the reactions.

Also, many organic chemists have made considerable effort to substitute organic solvents in organic synthesis with aqueous solvents owing to their safe, eco-friendly and non-toxic properties [33–38]. For the reactions in aqueous media, Yang et al. reported a PEG-coated resin-supported palladium catalyst for Suzuki cross-coupling reaction [34]. Nakao et al. reported an amphiphilic resin-supported palladium catalyst for cross-coupling reaction in aqueous conditions [35]. However, phase transfer reagents such as TBAB (tetrabutylammonium bromide) [39–41], polyethylene glycol (PEG) [42,43] or polar organic co-solvents [44–52] such as *N,N*-dimethylformamide are usually needed to improve the solubility of organic substrates in water [53]. For a more practical use of phase transfer reagents in aqueous media, Mukhopadhyay

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Scheme 1. Preparation of CS-g-mTEG or mPEG Pd (0) catalysts.

et al. reported the anchoring of TBAB to a Pd/C-supported catalyst for biphenyl synthesis [54]. Paetzole et al. reported CTAB (cetyltrimethylammonium bromide) loaded mesoporous supports with embedded Pd catalyst [55]. Despite the fact that the supported phase transfer reagents showed better activity, there are still reusability and recovery issues that need to be addressed.

In our previous work, ligand-free chitosan-supported palladium (0) catalysts (CS-Pd (0) catalyst) were prepared and applied to the Suzuki cross-coupling reaction in water [56]. However, the use of TBAB was essential to obtain a high yield of biphenyl products as it improved the solubility of the organic substrates in an aqueous solvent and accelerated the rate of cross-coupling via the formation of a boronate complex $[\text{ArB}(\text{OH})_3]^- [\text{R}_4\text{N}]^+$ [40].

In this paper, we anchored mono-methoxy triethylene glycol (mTEG) or mono-methoxy polyethylene glycol (mPEG) as phase transfer reagents, to the CS-Pd (0) catalyst because PEG is water-compatible and thermally stable [42,43]. Thus, chitosan-g-mTEG or mPEG-supported palladium (0) catalyst (CS-g-mTEG or mPEG Pd (0) catalyst) was used in the Suzuki cross-coupling reaction in water without phase transfer reagents. The catalyst showed good catalytic activity and reusability.

2. Experimental

2.1. General remarks

Chitosan (Mw 40 000–50 000, deacetylation 98%) was purchased from Dong Bang Chito Bio Co. (Korea). All reagents and solvents are commercially available. ^1H NMR spectra were recorded at 300 MHz in deuterated DMSO on a JEOL JNM-LA300 spectrometer (Japan). The purity of biphenyl products from Suzuki cross-coupling reaction was obtained by its GC–Mass (HP 6890 GC system and HP 5973 Mass Selective Detector, USA). Field emission scanning electron microscope (FE-SEM) images of the catalyst were obtained from JEOL JSM-6700F (Japan) with energy dispersive X-ray (EDX) spectrometer. Energy filtering transmission electron microscope (EF-TEM) images were collected from Carl Zeiss LIBRA 120 (Germany).

2.2. Preparation of cross-linked CS-Pd (0) catalyst

CS-g-mTEG or mPEG Pd (0) catalysts were prepared by grafting mTEG or mPEG as in Scheme 1. CS-Pd (0) catalyst was prepared as our previous method [56]. To “tie and tangle” the beads with amino groups on the bead surfaces and strengthen the chemical

and physical stability of the CS-Pd (0) catalysts, the catalysts were cross-linked using glutaraldehyde. This process allows permanent arrest of the palladium particles on or in the beads without the use of a supporter such as ligands or a stabilizer.

For cross-linking, 20 mL of the CS-Pd (0) catalysts was reacted with 1.25 mL of a 25% glutaraldehyde aqueous solution (3.32 mmol) in a citric acid buffer (80 mL, pH 5.5). After shaking for 2 h at 25 °C, the CS-Pd (0) catalyst was washed with water. The imine groups, resulted from this process, were reduced using NaBH_4 to prevent hydrolysis. It was treated with 80 mL of 0.5% NaBH_4 (400 mg) in a boric acid buffer (80 mL, pH 9.0) for 1 h at 25 °C and washed with water, ethanol, and *N,N*-dimethylformamide (DMF).

2.3. Preparation of triazine-grafted CS-Pd (0) catalyst

For grafting mTEG or mPEG [57], the cross-linked CS-Pd (0) catalysts (20 mL) were treated with 2,4,6-trichlorotriazine (1.83 g, 3 eq.)

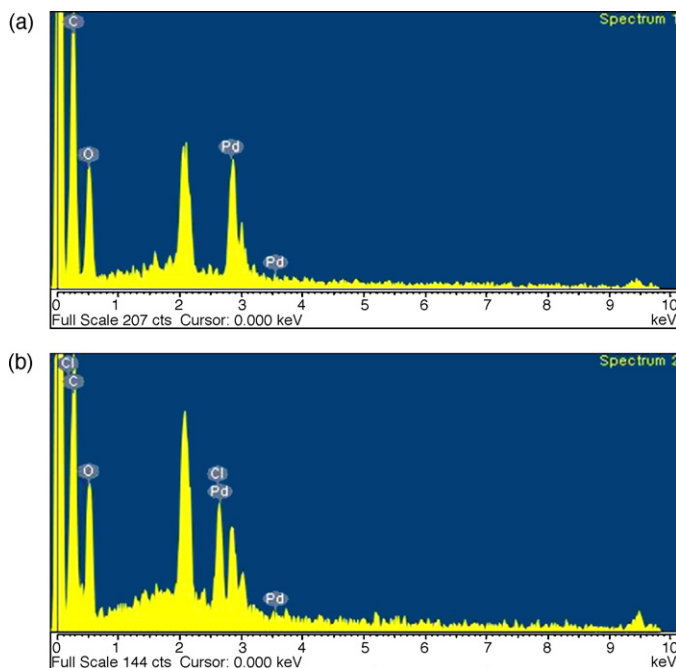


Fig. 1. SEM-EDX images of the catalysts: (a) CS-Pd (0) catalyst; (b) CS-g-mPEG350 Pd (0) catalyst.

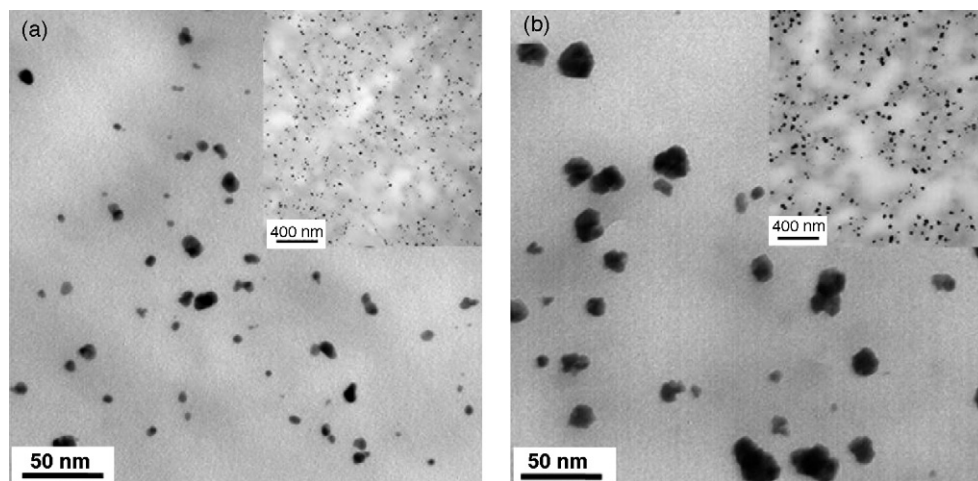


Fig. 2. TEM image of cross-sectioned catalysts: (a) CS-Pd(0) catalyst; (b) CS-g-mPEG350 Pd(0) catalyst.

and *N,N*-diisopropylethyl amine (DIPEA, 1.45 mL, 3 eq.) in 80 mL of DMF. The mixture was then stirred at 30 °C for 10 h and the catalyst was filtered and washed with DMF, ether, acetone to remove the residual 2,4,6-trichlorotriazine and other reagents. We confirmed that the resulting CS-Pd(0) catalyst (C: 35.5%, H: 5.5%, and N: 12.7%) was reacted with triazine by elemental analysis (for cross-linked CS-Pd(0) catalyst, C: 36.2%, H: 5.5%, and N: 5.9%).

2.4. Preparation of CS-g-mTEG or mPEG Pd(0) catalyst

To graft mTEG or mPEG (Mw 350 or Mw 750) to the position of the remaining chlorides of triazine, the triazine-grafted CS-Pd(0) catalysts (6.67 mL) were reacted with mTEG (0.5 g), mPEG350 (1.05 g) or mPEG750 (2.24 g). As follows, mTEG or mPEG was added to the triazine-grafted CS-Pd(0) catalyst in polypropylene tubes with a frit (Shimadzu Libra tube, Japan, 20 mL) with 15 mL of pyridine. The mixture was shaken at 60 °C for 19 h. After filtration and washing with ether, acetone, ethanol and water, the catalysts were freeze-dried for 24 h. The resulting CS-g-mTEG or mPEG Pd(0) catalysts were applied to the Suzuki cross-coupling reaction in water.

2.5. Application to the Suzuki cross-coupling reaction in water

The resulting CS-g-mTEG or mPEG Pd(0) catalysts were applied to the Suzuki cross-coupling reaction and the results were compared that of the CS-Pd(0) catalyst. The reactions were carried out in sealed vessels to prevent the loss of water due to the high

reaction temperatures (150 °C). [40,56] CS-g-mTEG or mPEG Pd(0) catalysts (0.5 mol%), phenylboronic acid (96 mg, 0.75 mmol), aryl halides (0.5 mmol) and various bases (1.5 mmol) were added to the vessel (10 mL) with 4 mL of water. The reaction mixture was continuously stirred in the vessels at 150 °C for 1–6 h under conventional heating. After cooling the solution to room temperature, the catalyst was filtered and washed with chloroform and water. The product was separated from the solution by extraction with chloroform and was purified by flash column chromatography (*n*-hexane:chloroform). Isolation yields were calculated from the mass of the purified biphenyl products. All isolated products were confirmed by ¹H NMR and GC–Mass and were demonstrated to be more than 99% pure by GC.

3. Results and discussion

3.1. Characterization of CS-Pd(0) catalyst and CS-g-mTEG or mPEG Pd(0) catalyst

The existence of palladium in the chitosan beads was confirmed by SEM-EDX analysis (Fig. 1). Also, chloride was detected for CS-g-mTEG or mPEG Pd(0) catalyst which means triazine was successfully reacted with hydroxyl groups on chitosan bead and some unreacted chlorides are left in grafting mTEG or mPEG step. The appearance of the CS-Pd(0) catalyst and CS-g-mTEG or mPEG Pd(0) catalyst is different in color. The former was black and the latter was grey.

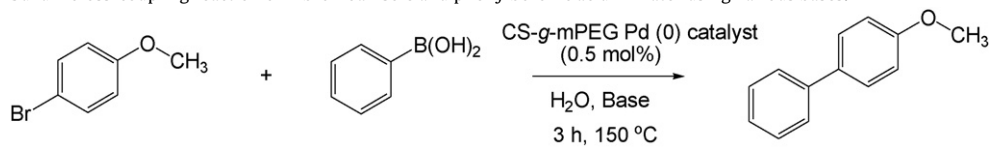
Table 1
Suzuki cross-coupling reaction of 4-bromoacetophenone and phenylboronic acid in water using various CS-g-mTEG or mPEG Pd(0) catalysts.^a

Entry	Catalyst	TBAB	Yield ^b (%)
1	CS-Pd(0)	×	28
2	CS-Pd(0)	1 eq.	95
3	CS-g-mTEG Pd(0)	×	84
4	CS-g-mPEG350 Pd(0)	×	92
5	CS-g-mPEG750 Pd(0)	×	91

^a Conditions: 0.5 mmol of 4-bromoacetophenone, 0.75 mmol of PhB(OH)₂, 1.5 mmol of K₃PO₄, 4 mL of water.

^b The yields were determined from the mass of biaryl products after flash column chromatography.

Table 2
Suzuki cross-coupling reaction of 4-bromoanisole and phenylboronic acid in water using various bases.^a



Entry	Base	Yield ^b (%)
1	CS ₂ CO ₃	35
2	Na ₂ CO ₃	47
3	NaOH	51
4	K ₂ CO ₃	49
5	K ₃ PO ₄	48

^a Conditions: 0.5 mmol of 4-bromoanisole, 0.75 mmol of PhB(OH)₂, 1.5 mmol of base, 4 mL of water.

^b The yields were determined from the mass of biaryl products after flash column chromatography.

The grafting yields calculated from the mass increases were 14.2 mol%, 7.0 mol% and 3.3 mol% for mTEG, mPEG350 and mPEG750, respectively. At this point, we concluded that mTEG or mPEG was successfully grafted as we intended.

An EF-TEM study was performed to reveal the existence of palladium nanoparticles in the catalysts (Fig. 2). From the cross-sectioned images of CS-Pd (0) catalyst or CS-g-mPEG350 Pd (0) catalyst, we found that the palladium nanoparticles were larger (15 nm) in the CS-g-mPEG350 Pd (0) catalyst than in the CS-Pd (0) catalyst (5 nm). We assumed that it might have been resulted from the longer preparation time for grafting triazine and mTEG or mPEG.

The palladium loading was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The palladium loading in the CS, CS-g-mTEG, CS-g-mPEG350 and CS-g-mPEG750 Pd (0) catalyst was 1.14 mmol/g, 0.71 mmol/g, 0.73 mmol/g and 0.89 mmol/g, respectively. The decreases in Pd loading when mTEG or mPEG was grafted might be caused by the increases in mass of the bead. Nevertheless, the palladium loading was much higher than those of the polystyrene based catalysts used in our previous study [36,45,46] due to the high metal sorption capacity of chitosan.

3.2. Suzuki cross-coupling reaction with the catalysts in water

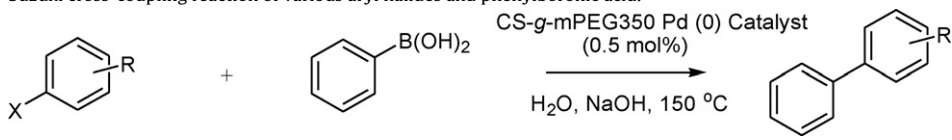
The resulting CS-Pd (0) catalyst and CS-g-mTEG or mPEG Pd (0) catalyst were applied to the Suzuki cross-coupling reaction. 4-Bromoacetophenone and phenylboronic acid were reacted for 1 h with various catalysts (0.5 mol%) as shown in Table 1, under con-

ventional heating conditions with continuous stirring. The results of the Suzuki cross-coupling reaction with the CS-Pd (0) catalyst were similar to those reported in our previous work (Table 1, entries 1 and 2) [56]. The activity of CS-g-mTEG or PEG Pd (0) catalyst was similar to the one of the CS-Pd (0) catalyst when TBAB was used as a phase transfer reagent (Table 1). Without using TBAB, the activity of the CS-g-mPEG Pd (0) catalyst was superior to that of the CS-Pd (0) catalyst (Table 1, entries 3–5). For comparing this result to our previous one, we also carried out the reaction of 4-bromoacetophenone and phenylboronic acid under microwave heating with CS-g-mPEG350 Pd (0) catalyst. The product yield of biphenyl from 15 min reaction was similar to the one from 1 h reaction under conventional heating. These results demonstrate that grafted mTEG or mPEG worked as an effective phase transfer reagent in the Suzuki cross-coupling reaction in water. In addition, these results showed that a longer mPEG chain is necessary because the CS-g-mTEG Pd (0) catalyst gave a lower yield (84%) relative to the other catalysts with longer mPEG chains (>90%).

3.3. Optimal reaction conditions for CS-g-mPEG Pd (0) catalyst

In order to determine the optimal reaction conditions, various types of bases were screened because the initially attempted phosphate base interfered with the separation of the catalyst by forming clots during the reaction. Among the bases examined in the reaction of 4-bromoanisole and phenylboronic acid, sodium hydroxide was found to be most suitable because it gave the highest product yield (Table 2, entry 3) without forming clots during the reaction.

Table 3
Suzuki cross-coupling reaction of various aryl halides and phenylboronic acid.^a

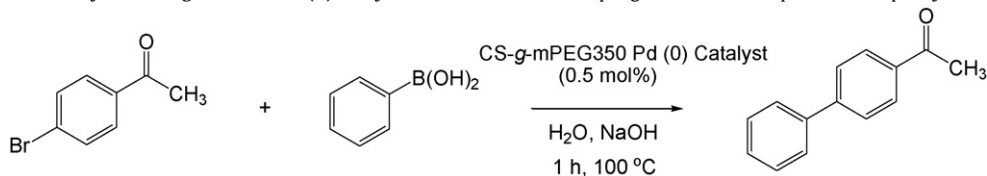


Entry	R	X	Time (h)	Yield ^b (%)
1	<i>p</i> -COCH ₃	I	0.33	92 ^c
2	<i>p</i> -OCH ₃	I	3	95
3	<i>p</i> -CH ₃	I	3	66
4	<i>p</i> -H	I	1	81
5	<i>p</i> -COCH ₃	Br	1	92 ^c
6	<i>p</i> -OCH ₃	Br	5	77
7	<i>p</i> -CH ₃	Br	5	66
8	<i>p</i> -H	Br	2	79
9	<i>p</i> -COCH ₃	Cl	3	55
10	<i>p</i> -H	Cl	3	13

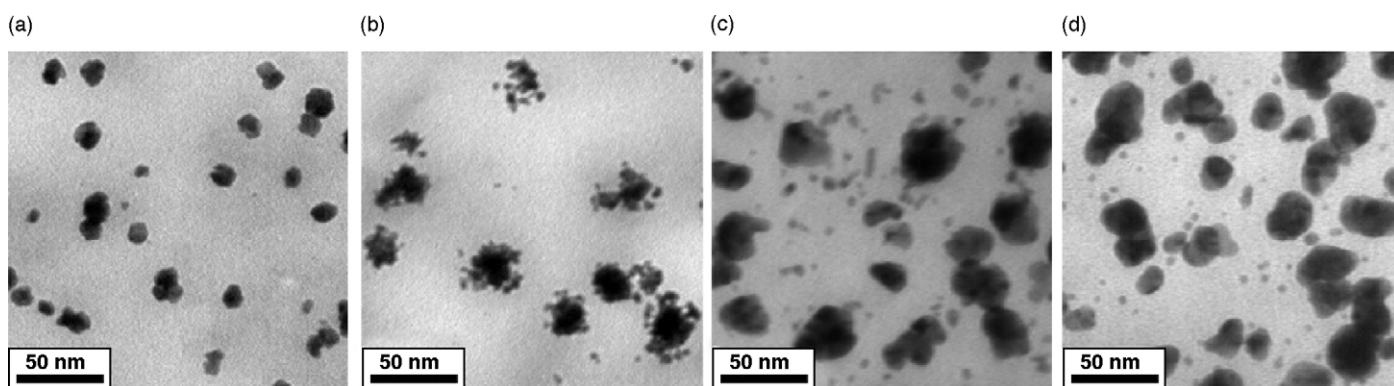
^a Conditions: 0.5 mmol of aryl halide, 0.75 mmol of PhB(OH)₂, 1.5 mmol of NaOH, 4 mL of water.

^b The yields were determined from the mass of biaryl products after flash column chromatography.

^c 100 °C.

Table 4Reusability of the CS-g-mPEG350 Pd (0) catalyst for the Suzuki cross-coupling of 4-bromoacetophenone and phenylboronic acid in water.^a

The number of reuse	Run A		Run B	
	Reaction time (h)	Yield ^b (%)	Reaction time (h)	Yield ^c (%)
1st	1	96	1	92
2nd	1	87	2.5	86
3rd	1	54	3	85
4th	1	50	3.5	88
5th	1	53	4	93
6th	2	62	–	–

^a Conditions: 0.5 mmol of 4-bromoacetophenone, 0.75 mmol of PhB(OH)₂, 1.5 mmol of NaOH, 4 mL of water.^b GC yield by GC–Mass.^c The yields were determined from the mass of biaryl products after flash column chromatography.**Fig. 3.** TEM images of the cross-sectioned catalysts: (a) CS-g-mPEG350 Pd (0) catalyst; (b) after 1 h; (c) after 3 h; (d) after 6 h.

3.4. Suzuki cross-coupling reaction of various aryl halides

As the catalytic activity of CS-g-mPEG350 Pd (0) catalyst was similar to that of CS-g-mPEG750 Pd (0) catalyst, the Suzuki cross-coupling reactions of various aryl halides were carried out using the CS-g-mPEG350 Pd (0) catalyst. Aryl iodides produced the coupling products close to 90% yield, except for 4-iodotoluene (66%, Table 3, entries 1–4). The aryl bromides gave viable product yields (66–92%, Table 3, entries 5–8). For aryl chlorides, 4-chloroacetophenone gave a 55% product yield (Table 3, entry 9) despite the fact that aryl chlorides are especially hard to be coupled with phenylboronic acids in water. Overall, the CS-g-mPEG350 Pd (0) catalyst showed excellent catalytic activity in the Suzuki cross-coupling reaction without the need for phase transfer reagents in water.

3.5. Reusability test of CS-g-mPEG350 Pd (0) catalyst

The feasibility of recycling the CS-g-mPEG350 Pd (0) catalyst was also examined. After the reaction, the catalyst was simply recovered by filtration and washing. However, the catalytic activity kept decreasing until the third reuse and was maintained to some extent thereafter.

The reaction solutions were analyzed by ICP-AES after every run to determine the amount of palladium leaching during the reaction. The total amount of palladium leaching after the 5th run was <5%. Comparing to previous results by our group [46,56], it is believed that the amount of Pd leaching of the CS-g-mPEG350 Pd (0) catalyst during the reaction was not a key factor in decreasing the

catalytic activity. Therefore, the cross-sectioned TEM images of the CS-g-mPEG350 Pd (0) catalyst were analyzed after various reaction times. From the TEM images, it was found that the size of the impregnated palladium (0) nanoparticles inside the beads had increased from 5–15 nm to 20–30 nm after 3 h reaction. However, no further severe aggregations occurred after the third reuse (Run A in Table 4), which corresponds to the result of the 3 h reaction (Fig. 3c). Subsequently, there was a decline in the rate of decreasing catalytic activity (Fig. 3d, Run A in Table 4).

Therefore, it was reasoned that the decrease in catalytic activity was resulted from the aggregation of palladium nanoparticles [58,59]. A longer reaction time was used to compensate for the decreased activity, resulting in an increase in coupling yield (Run B in Table 4).

4. Conclusions

For the Suzuki cross-coupling reaction in aqueous media, CS-g-mTEG or mPEG Pd (0) catalysts were prepared by simple steps with a high palladium loading and good catalytic activity. The catalysts were characterized and successfully applied to the Suzuki cross-coupling reaction. From the results of the reaction in water, we concluded that the grafted PEG chain acted as an effective solubilizing agent for the organic substrates in aqueous media. Using the CS-g-mPEG Pd (0) catalyst, aryl chloride was more easily coupled in water. Therefore, they showed better catalytic activity than the non-grafted one (CS-Pd (0) catalyst). Also, the CS-g-mPEG350 Pd (0) catalyst was reused up to five times. However, the catalytic

activity of the CS-g-mPEG350 Pd(0) catalyst was decreased to some extent. This might be due to the aggregation of palladium nanoparticles inside the chitosan beads during certain period of exposure time to high reaction temperatures. As we increased the reaction time, we were able to obtain high product yield.

Acknowledgements

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