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# A simple catalyst for aqueous phase Suzuki reactions based on palladium nanoparticles immobilized on an ionic polymer

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Palladium nanoparticles immobilized on a cross-linked imidazolium-containing polymer were evaluated as a catalyst for Suzuki carbon-carbon cross-coupling reactions using water as the solvent. The nanocatalysts show good catalytic activities for aryl iodides and aryl bromides and moderate activity with aryl chloride substrates. Coupling of sterically hindered substrates could also be achieved in reasonable yields. The heterogeneous catalyst is stable, can be stored without precautions to exclude air or moisture, and can be easily recycled and reused.

catalysis, biphasic catalysis, polymeric ionic liquids, nanoparticles, aqueous phase catalysis, Suzuki reaction

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# 1 Introduction

The Suzuki-Miyaura cross-coupling reaction of aryl halides with aryl boronic acids is one of the most versatile synthetic routes employed in organic chemistry for the generation of biaryl structures [1,2]. In general, molecular catalysts almost exclusively based on palladium(0), e.g.  $Pd(PPh_3)_4$  or palladium(0) catalysts generated *in situ* from palladium(II) salts, e.g.  $Pd(PPh_3)_2Cl_2$ , in donor solvents such as tetrahydrofuran (THF) or dioxane [3–5] are used as pre-catalysts in this reaction. Increasingly, palladium nanoparticles are also employed for these coupling reactions, although it is generally accepted that the nanoparticles act as catalyst reservoirs affording palladium(0) single atom species that are the actual active catalysts [6].

Despite this mechanism involving an interplay between heterogeneous and homogeneous entities, the development of efficient heterogeneous catalysts for the Suzuki reaction attracts much interest, as they facilitate product purification and enable facile catalyst recovery and recycling. Palladium nanoparticles immobilized on many different types of supports, including zeolites [7,8], silica [9,10], dendrimers [11,12], magnetic beads [13,14] and other materials [15–17] have been reported. In addition to the development of heterogeneous catalysts, the use of alternative solvents to the volatile organic solvents typically used for the Suzuki reaction has also been considered. Notably, ionic liquids have attracted a lot of attention as reaction solvents as they are stable, non-volatile and can facilitate product separation and catalyst recycling [18-20]. A number of functionalized ionic liquids have been developed for cross-coupling reactions although most are used together with water [21-24]. Water has also been extensively used as a solvent for Suzuki and other cross-coupling reactions [25-29].

Previously, we reported a polymeric ionic liquid derived from a styrene-functionalized imidazolium salt, i.e. 1-(4-

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vinylbenzyl)-3-methylimidazolium chloride, [vbim]Cl (Figure 1), termed poly[vbim]Cl, able to stabilize gold nanoparticles in both ionic liquids [30] and in aqueous media [31]. The solubility properties of the polymeric ionic liquid may be modulated by exchange of the counter-anion. For example, with the chloride counter-ion the polymer and the corresponding polymer coated metal nanoparticles are hydrophilic, whereas with bis(trifluoromethylsulfonyl)imide, [Tf<sub>2</sub>N], they become hydrophobic. Palladium nanoparticles coated with the latter polymer, i.e. poly[vbim][Tf<sub>2</sub>N], immobilized in an ionic liquid were shown to catalyze Suzuki reactions under relatively mild conditions [32].

By attaching a second vinyl-group to the imidazolium monomer, i.e. 1,3-bis(4-vinylbenzyl)imidazolium chloride, [bvbim]Cl (Figure 1) [33], a cross-linked polymer termed poly[bvbim]Cl is obtained [34]. This polymer is insoluble in most common solvents and it is highly thermal stable and was employed as an organocatalyst for the cycloaddition of carbon dioxide to epoxides.

Herein, we describe the preparation and characterization of palladium nanoparticles immobilized on poly[bvbim]Cl. The resulting material was investigated as a heterogeneous catalyst in Suzuki cross-coupling reactions in aqueous media.

# 2 Experimental

# 2.1 General

Chemicals were obtained from commercial sources and used without further purification. The polymer ionic liquid, poly[bvbim]Cl, was prepared according to a literature procedure [33]. Transmission electron microscopy (TEM) was performed on a Philips CM-12 TEM instrument (Netherlands) with a LaB6 source operated at 120 kV. Samples for TEM analysis were prepared by adding the Pd-NP-PIL catalyst suspension to isopropanol, followed by ultrasonication for 30 min. A few drops of the suspension were then placed onto a carbon film coated Cu grid which was then dried for 1 h under an infrared lamp. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Perkin-Elmer PHI 5000CESCA (USA) system with a base pressure of  $10^{-9}$  Torr. Inductively coupled plasma mass spectrometry (ICP-MS) was used to quantify the amount of



**Figure 1** Styrene functionalized imidazolium chloride monomers. (a) 1-(4-vinylbenzyl)-3-methylimidazolium chloride ([vbim]Cl); (b) 1,3-bis(4-vinylbenzyl)imidazolium chloride ([bvbim]Cl).

palladium in the Pd-NP-PIL catalyst. Samples were digested in concentrated nitric acid at 80 °C for 16 h and then water was added to a total volume of 7 mL. Indium was added as an internal standard at a concentration of 0.5 ppb. Determination of palladium content was achieved on a Perkin Elmer Elan DRC II ICP-MS instrument (USA) equipped with a Meinhard nebulizer and a cyclonic spray chamber. The ICP-MS instrument was tuned using a solution provided by the manufacturer containing 1 ppb of each element Mg, In, Ce, Ba, Pb and U. External standards were prepared gravimetrically in identical matrix to the samples (with regard to internal standard and nitric acid) with single element standards obtained from CPI International (Netherlands).

#### 2.2 Preparation of the Pd-NP-PIL catalyst

A mixture of PdCl<sub>2</sub> (47.4 mg, 0.268 mmol) and NaCl (313.2 mg, 5.36 mmol) in deionized water (7 mL) (Milli-Q, Millipore, USA) was heated at 80 °C until the entire quantity of PdCl<sub>2</sub> reacted to give a red solution of Na<sub>2</sub>[PdCl<sub>4</sub>]. The mixture was cooled to r.t. and poly[bvbim]Cl (0.250 g, 0.744 mmol based on the monomer) was added. The suspension was stirred for 20 h at r.t., filtered, and the precipitate was washed with water (3×5 mL) and dried for 16 h under vacuum at r.t.. The resulting orange powder was suspended in ethanol (7 mL) and a solution of NaBH<sub>4</sub> (70 mg, 1.87 mmol) in ethanol (7 mL) was added dropwise to afford a black suspension that was stirred at r.t. for a further 6 h. The suspension was filtered, the precipitate was washed with water (3×5 mL) and dried for 16 h under vacuum at r.t. The palladium content was determined by ICP-MS (0.0087 mmol Pd per 10 mg Pd-NP- PIL catalyst).

# 2.3 General procedure for the Suzuki coupling reactions

A mixture of aryl halide (0.5 mmol, 1.0 equiv.), phenylboronic acid (0.6 mmol, 1.2 equiv.),  $K_2CO_3$  (2 mmol, 4 equiv.), the Pd-NP-PIL catalyst (1.7 mol% based on the aryl halide substrate) in water (3 mL) was heated to 100 °C under nitrogen with vigorous stirring for 4 h. The reaction mixture was then cooled at r.t. and the product was extracted with diethyl ether (3×3 mL). The combined extracts were washed with brine (15 mL), dried over anhydrous MgSO<sub>4</sub>, filtered and the solution was analyzed by GC. The structure of the products was also confirmed by <sup>1</sup>H NMR spectroscopy.

## 2.4 Recycling studies

After each reaction the catalyst was separated from the reaction mixture by centrifugation, washed with water  $(3\times3 \text{ mL})$ , diethyl ether  $(3\times3 \text{ mL})$  and acetone  $(3\times3 \text{ mL})$  and further dried under vacuum for 18 h and used for another catalytic cycle as described in Section 2.3.

## 3 Results and discussion

The polymer ionic liquid poly[bvbim]Cl was reacted with Na<sub>2</sub>[PdCl<sub>4</sub>] (prepared *in situ* by the addition of NaCl to an aqueous solution of PdCl<sub>2</sub>) leading to the exchange of the chloride counter-anions in the polymer by the [PdCl<sub>4</sub>]<sup>2–</sup> anions. The resulting poly[bvbim][PdCl<sub>4</sub>] material was reacted with Na[BH<sub>4</sub>] to afford palladium nanoparticles trapped on the polymer surface, termed Pd-NP-PIL. The transmission electron microscopy (TEM) image of poly [bvbim]Cl shows a characteristic spherical (aggregated) shape (Figure 2). The TEM of the Pd-NP-PIL material shows palladium nanoparticles adhered to the surface of the polymer with diameters ranging from 2 to 5 nm (the spherical shape of the polymer is retained).

The catalyst (Pd-NP-PIL) was also characterized by X-ray photoelectron spectroscopy (XPS) (Figure 3). Peaks corresponding to both Pd(II) and Pd(0) species were detected (Figure 3(b)). The binding energies of 335.6 eV (Pd  $3d_{5/2}$ ) and 340.7 eV (Pd  $3d_{3/2}$ ) are related to fully reduced Pd nanoparticles, whereas the peaks at 337.7 eV (Pd  $3d_{5/2}$ ) and 343 eV (Pd  $3d_{3/2}$ ) suggest that a number of unreduced Pd<sup>2+</sup> ions are present in the catalyst. The results are in accordance with previous reports which show the palladium nanoparticles supported by polymers contain surface Pd<sup>2+</sup> species [35–37].

The Pd-NP-PIL material is insoluble in common solvents and is stable up to 350 °C and, consequently, was evaluated as a heterogeneous catalyst in Suzuki coupling reactions in aqueous solution at 100 °C using various aryl halide substrates (Table 1).

The Pd-NP-PIL catalyst efficiently converts aryl iodides and aryl bromides to biaryl products in the presence of phenylboronic acid in high yield using short reaction times (4 h) at low catalyst loadings (10 mg, 1.7 mol%). The Pd-NP-PIL catalyst in water tends to be superior to many catalysts that operate in ionic liquids [38,39]. Moreover, the Pd-NP-PIL catalyst is also able to couple aryl chloride substrates in modest yield (16%–23%). It is noteworthy that under comparable conditions most heterogeneous catalysts tend to give <5% yield [22,23,32].

The Pd-NP-PIL catalyst was also evaluated in the crosscoupling of more sterically hindered substrates (Table 2).



**Figure 2** Transmission electron microscopy images of poly[bvbim]Cl (a) and the Pd-NP-PIL material (b).



**Figure 3** (a) XPS survey spectrum of Pd-NP-PIL; (b) XPS spectrum of palladium 3d (color online).

 Table 1
 Suzuki cross-coupling reactions between phenylboronic acid and various aryl halides catalyzed by Pd-NP-PIL<sup>a)</sup>

$R - X + (HO)_{2}B - X + (HO)_{2}B - R - R - R - R - R - R - R - R - R - $		
Entry	R, X	Yield <sup>b)</sup> (%)
1	H, I	98
2	Me, I	93
3	MeO, I	99
4	NO <sub>2</sub> , I	99
5	CN, I	97
6	Me, Br	70
7	MeO, Br	99
8	NO <sub>2</sub> , Br	92
9	CN, Br	98
10	Me, Cl	23
11	MeO, Cl	17
12	CN, Cl	16

a) Reaction conditions: aryl halide/phenylboronic acid/K<sub>2</sub>CO<sub>3</sub> 1:1.2:4, catalyst Pd-NP-PIL (10 mg, 1.7 mol%), water (3 mL), T=100 °C, t=4 h; b) yield determined by GC.

Good yields were obtained for the methyl-substituted biaryl product whereas the dimethyl-product was obtained in only moderate yield. Nevertheless, under the conditions employed

Table 2 Suzuki cross-coupling of sterically hindered substrates catalyzed by Pd-NP-PIL  $^{a)}$ 



a) Reaction conditions: aryl halide/boronic acid/K<sub>2</sub>CO<sub>3</sub> 1:1.2:4, Pd-NP-PIL (10 mg, 1.7 mol%), water (3 mL), T=100 °C, t=4 h; b) yield determined by GC.

and in the presence of a cheap and inexpensive base the yields obtained are comparable or even superior to other heterogeneous catalysts [24,32,40].

The ability to reuse the Pd-NP-PIL catalyst was investigated using two different aryl iodide substrates. For both substrates good recyclability was observed over 5 catalytic runs with >90% of the original activity retained (Figure 4). The amount of palladium leached from catalyst was determined by ICP analysis after each catalytic run employing iodobenzene as the substrate. The leaching tests revealed that the amount of palladium in solution is <0.3% of the total Pd content.

The structure of the Pd-NP-PIL catalyst after 5 batches from the reaction of iodobenzene and phenylboronic acid was studied by TEM (Figure 5). Compared to the freshlyprepared catalyst (Figure 2) the structures are essentially the same, although the size of the palladium nanoparticles is slightly larger, demonstrating the high stability of the catalyst. Such stability is unusual, especially given the likelihood that the active catalyst corresponds to mononuclear palladium species extracted from the palladium nanoparticles, and hence it is not unreasonable that as the palladium species reattach to the nanoparticle surface after reaction agglomeration is observed.



Figure 4 Recycling of the Pd-NP-PIL catalyst. Reaction conditions: aryl halide/phenylboronic acid/K<sub>2</sub>CO<sub>3</sub> 1:1.2:4, Pd-NP-PIL (10 mg, 1.7 mol%), water (3 mL), T=100 °C, t=4 h.



Figure 5 The Pd-NP-PIL catalyst after 5 catalytic runs from the reaction of iodobenzene and phenylboronic acid.

## 4 Conclusions

In conclusion, we have prepared a highly robust and active heterogeneous catalyst for Suzuki cross-coupling reactions that operates in water in the presence of an inexpensive base. The catalyst is simple to prepare, stable for prolonged periods, and easy to use and recycle.

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**Conflict of interest** The authors declare that they have no conflict of interest.

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