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Introduction

Biaryl ketones are multipurpose building blocks in the field of pharmaceuticals, natural products, agrochemicals and biologically active compounds.1 Among many synthetic welldocumented methods, Friedel-Crafts acylation of substituted aromatic rings² and the acylation of aryl metal species with functional carboxylic acid derivatives3 are two usual approaches. But the former is incompatible with many functional groups due to using Lewis acids, and the latter could not avoid the formation of biaryl side products. The palladiumcatalyzed carbonylative Suzuki coupling reaction of aryl halides or triflates, carbon monoxide (CO) and aryl boronic acids (or aryl metal reagents) is an attractive route for the synthesis of biaryl ketones.⁴ Although the palladium-catalyzed three component cross-coupling reactions have been reported extensively,⁵ most of them were homogeneous without any consideration of recyclability and separation of catalyst and product, which limited their applications. In this context, it is desirable to develop heterogeneous and ligand free palladium catalysis protocols. Immobilization of the palladium

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Palladium nanoparticles immobilized onto supported ionic liquid-like phases (SILLPs) for the carbonylative Suzuki coupling reaction[†]

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Crosslinked polymeric materials based on poly(ionic liquid)s, also named supported ionic liquid-like phases (SILLPs) were prepared by copolymerization of dication imidazole ionic liquids with divinylbenzene (DVB). Using the SILLPs-related polymeric materials as supports, palladium (Pd) metal nanoparticles were immobilized and stabilized, which can efficiently catalyze the carbonylative Suzuki coupling reaction of aryl iodides with aryl boronic acids, affording the corresponding products in good to excellent yields. The Pd nanoparticles immobilized onto SILLPs were characterized by transmission electron microscopy (TEM), thermogravimetric analysis (TG), and X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR). The size and dispersion of the Pd nanoparticles supported on polymers are influenced possibly by varying the contents of the ionic liquid units and the introduction of amine groups. Furthermore, hot filtration and mercury poisoning tests indicated that the palladium species leached into the solvent during the reaction and returned to the polymers after the reaction was completed. In addition, the catalyst was easily recovered from the reaction mixture by filtration and reused over five consecutive cycles without a significant decrease in its activity.

nanoparticles on suitable supports to prepare heterogeneous catalysts has attracted much attention in the field of catalysis. Different supports have been used to stabilize the nanoparticles, such as carbon,⁶ silica,⁷ molecular sieves⁸ and polymers.⁹

Recently, ionic liquids (ILs) have been one of interesting subjects of scientific study because of their interesting and potentially useful physicochemical properties, including high ion conductivity, chemical stability, non-flammability and near absence of vapor pressure.^{10,11} ILs are proving to be an excellent 'green' solvent with significant potential for the traditional organic synthesis and catalytic reactions.12 Although ILs have become commercially available, they are still relatively expensive compared with traditional solvents. Nowadays, the immobilization of ILs onto a solid support, which providing a simple way for reducing the amount of IL, has been widely investigated.13 The immobilized ionic liquids as catalyst supports not only take advantage of excellent physicochemical properties of ionic liquid, but also realize recycling catalysis and ease catalyst-product separation.14 Many immobilized ionic liquids have been used to stabilize Pd catalysts. For example, Babak Karimi and coworkers anchored an imidazolium ionic liquid bearing triethylene glycol moieties on the surface of silicacoated iron oxide nanoparticles as Pd catalyst support, which could recover Pd catalyst magnetically.15 Recently, Martínez and coworkers used laponite clay to immobilize ionic liquid [bmim] $[PF_6]$, and then Pd nanoparticles were stabilized into it. The

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resulting catalysts showed excellent catalysis activity and recyclability for the Mizoroki-Heck reaction.¹⁶

The immobilization of ILs onto a solid support is often realized by either covalent or noncovalent bonds using various methods, including simple physisorption, self-assembly or polymerization. Poly(ionic liquid)s, also called polymerized ionic liquids or polymeric ionic liquids, refer to polymeric compounds that feature an IL species in each monomer repeating unit, connecting through a polymeric backbone, which are obtained by polymerization of ILs having polymerizable groups.¹⁷ The major advantages for such polymeric forms of ILs are enhanced stability, improved processability, flexibility, and durability in applications. Obviously, the crosslinked polymeric materials based on poly(ionic liquid)s, also named supported ionic liquid-like phases (SILLPs), in which the IL-like fragment is covalently attached to the support is better.¹⁸

The framework of our continuous efforts is to develop effective and green processes for the carbonylative coupling reaction.¹⁹ In this paper, we report the synthesis of two kinds of SILLPs based on dication imidazole ionic liquids supported palladium catalysts and illustrate its application in the carbonylative Suzuki coupling reaction to synthesize biaryl ketones without the addition of any phosphine ligands. The results demonstrated that the size and dispersion of the Pd nanoparticles in SILLPs are influenced by varying the contents of IL units and introduction of amine groups.

Results and discussion

Two kinds of SIILPs were prepared by the synthetic approaches outlined in Scheme 1. Differences between them focused mainly on whether dication imidazole ionic liquids were modified with amine groups. The SIILPs modified with amine groups were prepared based on the different DVB-NDIIL mole ratio. We obtained P(DVB¹-DIIL¹) and P(DVB^x-NDIIL¹) with x = 0.5, 1, 3, 6. The 'x' means the DVB-NDIIL mole ratio. Then the PdCl₄²⁻ as Pd precursor was absorbed in the polymers by ion exchange with halogen anion. After reduction by NaBH₄, the catalysts were denoted as P(DVB¹-DIIL¹)-Pd and P(DVB^x-NDIIL¹)-Pd. The exact contents of ILs in polymers were determined by element analysis, listed in Table 1. In order to investigate the effect of ionic liquid units, we fixed the input amount of Pd to be 2 wt%, and the exact loading amounts were determined by AAS, as shown in Table 1.

TEM was used to examine the size and size distribution of Pd nanoparticles supported on SIILPs (Fig. 1). The TEM images



Scheme 1 Synthesis of SIILPs immobilized Pd nanoparticles.

Element	$P(DVB^1-DIIL^1)$	P(DVB ⁶ -NDIIL ¹)	P(DVB ³ -NDIIL ¹)	$P(DVB^1-NDIIL^1)$	P(DVB ^{0.5} –NDIIL ¹)	
C (wt%)	50.6	84.9	71.0	56.8	50.8	
N (wt%)	9.75	1.9	8.8	12.6	14.7	
IL (mol%)	43	4	23	41	54	
Pd (wt%)	1.86	1.99	2.14	2.06	2.24	

Table 1 The data of element analysis of SIILPs and Pd contents

showed that the polymers modified with amine groups distributed Pd nanoparticles better than the one without amine groups. As shown in Fig. 1e, agglomeration apparently appeared on the P(DVB¹–DIIL¹), which was attributed to P(DVB¹–DIIL¹) not being modified with amine groups. P(DVB⁶–NDIIL¹) and P(DVB³–NDIIL¹) did not disperse Pd nanoparticles well, because there are not enough units of ILs with amine groups to stabilize

metal nanoparticles (Fig. 1f and g). Only when the proportion of ILs came up to a higher level, could Pd nanoparticles be dispersed well. P(DVB¹–NDIIL¹) and P(DVB¹–NDIIL²) had relatively high proportion of ILs, so we can see Pd nanoparticles disperse well on them (Fig. 1a and c), and the particle sizes are so small that the characteristic diffraction peaks of Pd are not observed under X-ray diffraction patterns. When we used these



Fig. 1 TEM and distribution of particle size images of the catalysts.



Fig. 2 The FT-IR spectra of polymers and catalysts.

five catalysts to catalyze carbonylative Suzuki coupling reaction of iodobenzene with phenyl boronic acid, the obtained yields were 56% [P(DVB¹–DIIL¹)–Pd], 49% [P(DVB⁶–NDIIL¹)–Pd], 79% [P(DVB³–NDIIL¹)–Pd], 85% [P(DVB¹–NDIIL¹)–Pd], 87% [P(DVB^{0.5}–NDIIL¹)–Pd]. On the one hand, the polymer P(DVB^{1–} NDIIL¹) prepared by DVB (mol)/NDIIL (mol) = 1 could disperse Pd nanoparticles very well. On the other hand, increasing content of NDIIL in polymers did not improve yield drastically. Therefore, in order to save expensive ionic liquid, we chose P(DVB¹–NDIIL¹)–Pd as catalyst to catalyze carbonylative Suzuki coupling reaction.

The polymer SIILPS, P(DVB¹–DIIL¹)–Pd and P(DVB¹– NDIIL¹)–Pd were characterized by FI-IR, and the results are shown in Fig. 2. Both spectra show an asymmetric broad band at around 3420 cm⁻¹, which is attributed to the stretching vibration of the C–H in imidazole rings and the N–H in amine groups. From Fig. 2a and b, we can see that the spectra are very similar before and after immobilizing Pd nanoparticles, suggesting that the structures of polymers remain intact. Fig. 2c shows that the broad bands at around 3420 cm⁻¹ become small gradually, which is consistent with the proportions of ionic liquid in polymers.

The polymers P(DVB¹–NDIIL¹) and catalyst P(DVB¹–NDIIL¹)– Pd were characterized by thermogravimetric analysis. The thermograms are shown in Fig. 3. The weight loss before 230 °C resulted from the loss of the adsorbed water. There were the



Fig. 3 The thermogram of $P(DVB^1 - NDIIL^1) - Pd$ and $P(DVB^1 - NDIIL^1)$.

pyrolysis of $P(DVB^1-NDIIL^1)$ and $P(DVB^1-NDIIL^1)-Pd$ appearing between 230 °C and 350 °C, which was attributed to the elimination of the dication ionic liquids immobilized on the polymers. The weight loss above 390 °C was due to the decomposition of PDVB. The results show that the catalyst can tolerate up to 230 °C.

The catalyst P(DVB¹–NDIIL¹)–Pd was used to catalyze carbonylative Suzuki reaction. In order to optimize the reaction

Table 2 The effect of reaction parameters on catalytic activity of carbonylative Suzuki–Miyaura reaction of iodobenzene with phenyl boronic $acid^a$

\bigcirc	+ CO +	B(Of	H) ₂ P(DVB ¹ -NDI Solvent, B	ase	°			
Entry	Solvent	Base	Time (h)	Temp (°C)	Yield ^b (%)			
The effect of the solvent								
1	Toluene	K_2CO_3	12	120	85			
2	Anisole	K_2CO_3	12	120	80			
3	THF	K ₂ CO ₃	12	120	46			
4	Acetonitrile	K_2CO_3	12	120	34			
5	Water	K_2CO_3	12	120	15			
6	NMF	K_2CO_3	12	120	20			
The eff	ect of the base							
7	Toluene	Na ₂ CO ₃	12	120	45			
8	Toluene	Cs_2CO_3	12	120	62			
9	Toluene	$\mathrm{Et}_{3}\mathrm{N}$	12	120	20			
The eff	ect of time							
10	Toluene	K_2CO_3	10	120	75			
11	Toluene	K ₂ CO ₃	8	120	64			
12	Toluene	K_2CO_3	14	120	85			
The eff	ect of CO press	sure						
13 ^c	Toluene	K_2CO_3	12	120	67			
14^d	Toluene	K ₂ CO ₃	12	120	86			
The eff	ect of temperat	ure						
15	Toluene	K ₂ CO ₃	12	100	61			
16	Toluene	K ₂ CO ₃	12	140	85			

^a Reaction conditions: iodobenzene (1 mmol), phenyl boronic acid (1.4 mmol), P(DVB¹-NDIIL¹)-Pd (1.0 mol%), base (3 mmol), solvent (10 mL), CO (3 MPa).
 ^b Isolated yield.
 ^c CO pressure 2 MPa.
 ^d CO pressure 4 MPa.

Table 3 Carbonylative Suzuki coupling reaction of aryl iodides with various aryl boronic acids^a





^{*a*} Reaction conditions: aryl iodide (1 mmol), aryl boronic acid (1.4 mmol), P(DVB¹–NDIIL¹)–Pd (1.0 mol%), K₂CO₃ (3 mmol), toluene (10 mL), CO (3 MPa), 120 °C, 12 h. ^{*b*} Isolated yield.

conditions, various reaction parameters such as solvent, base, reaction time, CO pressure and temperature were investigated, and the results are shown in Table 2. Firstly, the influence of different solvents on the carbonylative Suzuki coupling reaction was studied (Table 2, entries 1–6). According to the evaluated results of solvents, when nonpolar solvents, such as anisole and

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toluene, were used a relatively good yield of the carbonylative cross-coupling product, benzophenone, could be obtained. However, the yield of the carbonylative cross-coupling product was relatively low in polar solvents, such as THF, DMF, ethanol and water. These may be attributed to that nonpolar solvents are more advantageous to the C-I insertion than polar solvents, which is consistent with previous study.20 Next, we chose toluene as reaction solvent to screen suitable base (Table 2, entries 7-9). Compared with the organic base (Et₃N), the inorganic bases (Na₂CO₃, K₂CO₃ and Cs₂CO₃) showed better activities. Among the three inorganic bases, K₂CO₃ gave the best yields. We also investigated the effect of the pressure of CO, with decreasing the pressure of CO from 3 to 2 MPa, the yield decreased from 85 to 65%, respectively. However, with increasing the pressure of CO, the improving of the product yield was not observed (Table 2, entries 13 and 14), which might indicate that when the CO pressure came up to 3 MPa, continue to increase CO concentration played little role in reaction. In the case of temperature study, at 100 °C, the yield of the desired product was lower than the one at 120 °C (Table 1, entry 15). However, when the temperature increased to 140 °C, the yield of the desired product did not increase obviously (Table 1, entry 16), suggesting that in this catalysis system, 120 °C might reach the vertex of the catalyst activity. Therefore, the optimum reaction conditions for carbonylative Suzuki coupling reaction of iodobenzene with phenyl boronic acid were found to be: $P(DVB^1-NDIIL^1)-Pd$ (53 mg, 1.0 mol% relative to iodobenzene), toluene (10 mL) as solvent, K₂CO₃ (3 mmol) as base, under 3 MPa of CO pressure at 120 °C for 12 hours.

With the optimized reaction conditions, we extended the scope of carbonylative Suzuki reaction to a variety of different aryl iodides with various phenyl boronic acids. As shown in Table 3, various electron-donating and electron-withdrawing groups such as -Me, -OMe, -NH₂, -COMe, -NO₂, -OH, -Br and -Cl on both aryl iodide and aryl boronic acid smoothly underwent carbonylative Suzuki coupling reaction giving desired products with appreciable yields. Iodobenzene reacted with phenyl boronic acid giving 85% yield of benzophenone (Table 3, entry 1). It was observed that the p-iodoaryl with electron-donating groups such as -CH₃ and -OCH₃ gave excellent results (Table 3, entries 2 and 3) while iodoaryl with electron-withdrawing groups such as -NO2 and -COMe decreased the yields of the corresponding products (Table 3, entries 7 and 8). The iodoaryl with ortho-substituents also decreased the yield due to the steric effect (Table 3, entries 4-6). p-Chloroiodobenzene and o-bromoiodobenzene could react with phenyl boronic acid to convert into corresponding products, and excellent yields were obtained (Table 3, entries 9 and 10). Aryl boronic acids with various substituent groups were also investigated and the corresponding products were also obtained (Table 3, entries 11–18). It indicated that *p*-aryl boronic acids containing the electron-withdrawing groups, such as -Cl and -Br (Table 3, entries 11 and 12), produced relatively lower yields of the carbonylative coupling products than the ones with the electron-donating groups, such as -OCH₃ and -CH₃ (Table 3, entries 13 and 14). However, 3-methoxyphenylboronic acid did not improve the yield (Table 3, entry 15),

which may be attributed to that the methoxy group on *m*-position led to reduction of the electron density of C-1 position connecting with boronic acid. The reaction of sterically hindered *o*-tolylboronic acid with iodobenzene provided lower yield (57%) of the desired product compared with 3,5-dimethylphenylboronic acid, whose yield was 75% (Table 3, entries 16 and 17). Moreover, 2-naphthaleneboronic acid also reacted with iodobenzene, affording 79% yield of the corresponding ketone (Table 3, entry 18). It should be pointed out that the carbonylative coupling reaction of bromobenzene (or chlorobenzene) with phenyl boronic acid did not occur (Table 3, entries 19 and 20), because the dissociation energy of the C–Cl or C–Br bond is comparatively high (402, 339, and 272 kJ mol⁻¹ for PhCl, PhBr, and PhI, respectively, at 298 K).²¹

To obtain information about the heterogeneity or homogeneity of the catalytic reaction, hot filtration and mercury poisoning tests were carried out.²² At first, the relationship between the progress of reaction and time was depicted in Fig. 4 (reaction conditions: 1 mmol iodobenzene, 1.4 mmol phenyl boronic acid, 1.0 mol% P(DVB¹-NDIIL¹)-Pd, 3 mmol K₂CO₃, 10 mL toluene, 3 MPa CO, 120 °C), which revealed that the reaction rate was maximum at the range of 5-7 h. Thus, we chose the point of 6 h for the following experiments. The catalyst was filtered out at above 100 °C after the reaction proceeded for 6 h and the yield of benzophenone was 49% determined by GC. The obtained filtrate with additional 1.0 mmol phenyl boronic acid was continually stirred under the reaction conditions. After 10 hours the conversion was determined to be 56%. The same approach was applied to mercury test. After the first stage, the yield of benzophenone was 49%. In the second stage, after mercury (0.5 mL, 6.8 g) was added into the filtrate, the filtrate was stirred for another ten hours under the reaction conditions. The yield of benzophenone remained to be 49%. These phenomena show that a small amount of catalytically active palladium species may have leached to the reaction mixture. But the contents of Pd in catalyst before and after reaction were 2.06% and 2.04% respectively, determined by AAS. These indicate that most of Pd species leaching into



Fig. 4 Yield vs. reaction time plot for carbonylative Suzuki reaction of iodobenzene with phenyl boronic acid catalyzed by catalyst $P(DVB^1-NDIIL^1)-Pd$.



Fig. 5 Recyclability of P(DVB¹–NDIIL¹)–Pd catalyst in carbonylative Suzuki reaction of iodobenzene with phenyl boronic acid.

solution are recaptured onto the polymers after completion of the reaction. Furthermore, according to the recyclability experiment (Fig. 5), Pd recaptured by the polymers remained active when it was used in the next cycle. The results show that ionic liquid units grafted on the polymers provide a microenvironment analogous to ionic liquids so as to prevent the agglomeration of Pd nanoparticles. In addition, such results are consistent with the previous reports,²³ in which the Pd nanoparticles can realize the decoordination and coordination again in this system.

In order to evaluate the recyclability of the catalyst, the reusability was examined for the carbonylative coupling reaction of iodobenzene with phenyl boronic acid, and the results are presented in Fig. 5 (reaction conditions: 1 mmol iodobenzene, 1.4 mmol phenyl boronic acid, 1.0 mol% $P(DVB^1-NDIIL^1)-Pd$, 3 mmol K_2CO_3 , 10 mL toluene, 3 MPa CO, 120 °C, 12 h). The catalyst $P(DVB^1-NDIIL^1)-Pd$ could be reused effectively in five consecutive cycles, although the yield decreased slightly, which might be attributed to leaching of Pd and slight aggregation of the Pd nanoparticles (Fig. 1h). The content of Pd in catalyst after five cycles was 1.75 wt%, determined by AAS analysis.



Fig. 6 XPS spectrum of the Pd 3d edge of fresh and used catalyst $P(DVB^1-DIIL^1)-Pd$.

XPS spectra were measured for the catalyst $P(DVB^1-NDIIL^1)$ -Pd before reaction and after the 5th recycle, and the results are shown in Fig. 6. It can be seen that in the Pd 3d region, two peaks at 341.0 eV and 335.8 eV for $P(DVB^1-NDIIL^1)$ -Pd correspond to $3d_{5/2}$ and $3d_{3/2}$ for Pd(0) species. The peaks of 337.0 (Pd²⁺ 3d_{5/2}) and 342.2 eV (Pd²⁺ 3d_{3/2}) also appear in spectra, suggesting that a small number of unreduced Pd²⁺ ions still exist in catalyst. As for the catalyst after 5th recycle, the area of Pd²⁺ ions is smaller than the fresh one, suggesting that Pd²⁺ was slightly reduced by CO after 5th recycle.

Conclusions

In conclusion, SIILPs based on DVB and dication imidazole ionic liquids modified with amine groups were synthesized and proved to be an effective support for palladium nanoparticles. The precursor of Pd was adsorbed and dispersed effectively by ion-exchange of Cl^- for $PdCl_4^{2-}$. By comparison, amine groups modified in polymers are necessary for stabilizing Pd nanoparticles. Furthermore, a relatively high proportion of ionic liquid units in polymers is advantageous to disperse Pd nanoparticles. The Pd nanocatalysts immobilized on the ionic liquid polymers exhibited high catalytic activity in the carbonylative Suzuki coupling reaction of aryl iodides with aryl boronic acids. In addition, the catalyst could be easily separated from the products and recycled up to five consecutive times.

Experimental section

All chemicals are analytical grade. Divinylbenzene (DVB) was purchased from Alfa Aesar. *N*-Vinylimidazole, bis(2-chloroethyl) amine hydrochloride, 1,4-dibromobutane, aryl iodides and aryl boronic acids was provided by Energy Chemical. Na₂PdCl₄ was provided by Shanxi Kaida Chemical Engineering Co. Ltd. The other chemicals were purchased from Tianjin Kaitong Chemical Reagent Co. Ltd. The chemicals were used without further purification except azobis(isobutyronitrile) (AIBN) used after recrystallization.

Preparation of [(VIM)₂C₄N]Cl₂ (NDIIL)

To prepare the monomer 3,3'-(2,2'-azanediylbis(ethane-2,1diyl))bis(1-vinyl-1H-imidazol-3-ium)chloride (NDIIL), 1-vinylimidazole (11.3 g, 0.12 mol), bis(2-chloroethyl)amine hydrochloride (8.92 g, 0.05 mol) and ethanol (80 mL) were added to a flask equipped with a magnetic stirrer under an argon atmosphere. The mixture was refluxed at 90 °C for 4 days. Then, the white precipitate was centrifuged and washed by acetone (50 mL \times 3) and ethanol (50 mL \times 3). After drying at 40 °C under vacuum, 3,3'-(2,2'-azanediylbis(ethane-2,1-diyl))bis(1-vinyl-1Himidazol-3-ium)chloride hydrochloride was obtained. ¹H NMR $(400 \text{ MHz}, \text{MeOD}) \delta 9.54 \text{ (s, 2H)}, 8.04 \text{ (t, } J = 1.8 \text{ Hz}, 2\text{H}), 7.90 \text{ (t, } J$ = 1.8 Hz, 2H), 7.28 (dd, J = 15.6, 8.7 Hz, 2H), 5.97 (dd, J = 15.6, 2.7 Hz, 2H), 5.48 (dd, *J* = 8.7, 2.7 Hz, 4H), 4.80 (t, *J* = 5.9 Hz, 4H), 3.74 (t, J = 5.9 Hz, 4H), 3.30 (dt, J = 3.3, 1.6 Hz, 1H).¹³C NMR (101 MHz, MeOD) δ 137.71, 129.92, 124.66, 121.40, 110.70, 48.39, 46.99. Element analysis: C (44.9%), N (18.7%), H (7.2%).

Preparation of [(VIM)₂C₄]Br₂ (DIIL)

То prepare the monomer 1,4-butanediyl-3,3'-bis-lvinylimidazolium dibromine,24 1-vinylimidazole (9.42 g, 0.10 mol), 1,4-dibromobutane (10.80 g, 0.05 mol) and acetone (50 mL) were added to a flask equipped with a magnetic stirrer. The mixture was refluxed at 60 °C with stirring for over 24 h under an argon atmosphere. Then, the white precipitate was centrifuged and washed by acetone (30 mL \times 3) and chloroform (30 mL \times 3). After drying at 40 °C under vacuum, 1,4-butanediyl-3,3'-bis-l-vinylimidazolium dibromine was obtained. ¹H NMR (400 MHz, DMSO) δ 9.51 (s, 1H), 8.23 (t, J = 1.8 Hz, 1H), 7.94 (t, J= 1.7 Hz, 1H), 7.31 (dd, J = 15.6, 8.8 Hz, 1H), 5.97 (dd, J = 15.6, 2.4 Hz, 1H), 5.45 (dd, J = 8.7, 2.4 Hz, 1H), 4.26 (s, 2H), 1.85 (s, 2H). ¹³C NMR (101 MHz, DMSO) δ 135.45, 128.87, 123.23, 119.16, 108.68, 48.37, 25.69. Element analysis: C (41.3%), N (13.5%), H (6.7%).

Preparation of P(DVB-NDIIL)

To prepare P(DVB–NDIIL), DVB (1.302 g, 10.0 mmol), AIBN (0.10 g, 2 wt%) and NDIIL (3.66 g, 10.0 mmol) were dissolved in methanol (60 mL) under argon. The mixture was refluxed at 90 °C with stirring under argon.^{19a} After 12 h, a white solid was centrifuged and was washed with deionized water (50 mL \times 3) and methanol (50 mL \times 3). The final product was treated with equimolar NaOH and washed with water before being dried in vacuum at 80 °C for 12 h. The other polymers were synthesized with the desirable proportions under the same conditions.

Preparation of P(DVB-DIIL)

To prepare the DVB-cross-linked polymers, DVB (1.302 g, 10.0 mmol), AIBN (0.11 g, 2 wt%) and [(VIM)₂C₄]Br₂ (4.041 g, 10 mmol) were dissolved in DMSO (60 mL) under argon.^{19a} The mixture was refluxed at 75 °C with stirring under argon. After 12 h, a white solid was centrifuged and washed with deionized water (50 mL × 3) and methanol (50 mL × 3) before being dried in vacuum at 60 °C for 12 h.

Preparation of the catalysts

The process for synthesis of catalyst is schematically shown in Scheme 1. The metal precursor of Pd was adsorbed by ionexchange of Cl⁻ for PdCl₄²⁻. 0.5 g of ionic liquid polymer was dispersed in water and mixed with 28 mg Na₂PdCl₄.^{18a} After 10 h, the solid was then separated by centrifugation and washed several times by water. Finally, NaBH₄ (40 eq.) aqueous solution was slowly added to such a suspension mixture. After separation by centrifugation and washing several times with distilled water and ethanol, the catalysts were dried at 80 °C overnight in a vacuum oven. The catalyst was denoted as P(DVB¹–DIIL¹)–Pd or P(DVB^x–NDIIL¹)–Pd. The content of Pd in the catalyst was determined by using AAS.

Catalytic reaction

In the experiment, aryl iodide (1.0 mmol), aryl boronic acid (1.4 mmol), $P(DVB^x-NDIIL^1)-Pd$ (1 mol%), toluene (10 mL) and K_2CO_3 (3 mmol) were added to a 100 mL autoclave. After air was

replaced by CO, the autoclave was filled with 3 MPa CO. The reaction mixture was heated at 120 °C for 12 h. After reaction, the autoclave was cooled to room temperature and the remaining CO gas was carefully released. The autoclave was thoroughly washed with MeOH. The clear liquid was obtained by filtration and the carbonylative product was purified by column chromatography (silica gel, 100–200 mesh; petrol ether/ ethyl acetate = 10 : 1). All isolated products were characterized by FT-IR, ¹H and ¹³C NMR spectra. The spectral data of known compounds are consistent with those reported.^{25,26}

Procedure for recycle reaction

After reaction, the catalyst was obtained by centrifugation separation and washed with distilled water (10 mL \times 3) and methanol (10 mL \times 3). After dried under vacuum, the resulting catalyst was used for the next carbonylation reaction.

Characterization

Transmission electron microscopy (TEM) images were performed in a TECNAI G2 TF20 with a working voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) analyses of the catalysts were performed on a Thermon Scientific ESCALAB250xi spectrometer. NMR spectra were recorded on a Bruker Avance TM III spectrometer operating at 400 MHz for ¹H and 100 MHz for ¹³C with reference to tetramethylsilane (TMS) internal standard. The FT-IR spectra were collected on a Bruker IFS120HR spectrometer. The elemental analysis was detected by Element vario EL analyzer. X-ray photoelectron spectroscopy (XPS) data were obtained using an Thermo Fisher Scientific KAlpha ESCALAB 250Xi spectrometer. TG measurements were performed on a thermal analyzer (NETZSCH STA449F3) with a heating rate of 10 °C min⁻¹. Pd contents in the catalysts were examined by AAS analysis using contrAA700 made in Germany. High resolution mass spectrum (HRMS) were obtained on a Bruker Daltonics micro TOF-QII spectrometer. GC-MS were measured on an Agilent 7890/5795 GC-MS.

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