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Pd nanoparticles on a porous ionic copolymer: a highly active and recyclable catalyst for Suzuki–Miyaura reaction under air in water†Yanpeng Yu,^a Tongjie Hu,^{ab} Xiaorong Chen,^a Kunling Xu,^a Junli Zhang^a and Jun Huang^{*a}

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A porous copolymer of an IL with divinylbenzene was prepared and applied as a support for Pd nanoparticles. The supported Pd nanocatalyst was found to be extremely active for Suzuki–Miyaura reaction of aryl bromides and chlorides with phenylboronic acid even with 10 ppm Pd loading under air in water.

Ionic liquids (ILs) have received great attention in various fields due to their unusual properties, such as negligible vapor pressure and high thermal stability.¹ Imidazolium-based ILs exhibit dynamic locally heterogeneous environments, which allow their use as media for preparation of nanoparticles and for synthesis of other nanostructured materials.² Pd nanocatalysts in ILs were investigated extensively for hydrogenation and Heck reactions, and generally carbene ligands played an important role in the reaction systems.³ Pd catalyzed Suzuki–Miyaura reaction is of great importance in modern organic chemistry.⁴ Although various Pd/ligand systems have been reported for Suzuki–Miyaura reaction,⁴ industrial applications of the reaction remain challenging as the Pd/ligand systems are expensive and difficult to be recycled. Heterogeneous palladium catalysts are a promising option. There have been numerous supported Pd nanocatalysts reported for the Suzuki–Miyaura reaction, such as Pd nanoparticles on carbon,⁵ mesoporous zeolites,⁶ metal oxides and polymers.⁷ Nevertheless, the heterogeneous Pd catalyst has generally lower activity than that of its homogeneous counterpart. Moreover, the Pd atoms often leach out into solutions which limited the applications in practical use. To improve the activity and recyclability of heterogeneous Pd catalysts, some studies have been performed.^{6,8} But from a practical point of view, these Pd catalyst materials were not easy to be produced, especially in a large scale. Therefore, it is highly desirable to develop cheap and easy-produced heterogeneous Pd nanocatalysts with high durability and activity for Suzuki–Miyaura reaction.

The use of aryl bromides and chlorides was preferable as they are inexpensive and readily available for most cross-coupling reactions.⁹ The activation of aryl chlorides and

bromides is much more difficult than aryl iodides, thus the development of heterogeneous nanocatalysts that can activate aryl chlorides and bromides with high efficiency and durability was highly desirable. We have developed a general and efficient Pd catalyst system for C–O coupling of aryl bromides and chlorides with phenols recently,¹⁰ and we are interested in the development of practical Pd catalysts that can be used in laboratory as well as industrial scale. Based on the Pd nanocatalysts in ILs,¹¹ we attempt to develop a stable and active heterogeneous nanocatalyst for the coupling reactions.

Recently, polymeric ILs were developed and applied in transition metal catalysis with good performance.¹² However, these catalyst systems are limited with the problem of the mass transfer since the polymeric ILs are nonporous and insoluble in the reaction systems. Accordingly, porous polymeric ILs will be favorable and much more efficient for the related reactions. And herein we demonstrate a facile one-step synthetic strategy to a porous ionic copolymer (PIC) *via* radical copolymerization of an IL with divinylbenzene (DVB). With the immobilized IL material, we designed a heterogeneous Pd nanocatalyst system for Suzuki–Miyaura reaction, which showed extremely high activity and durability under air in aqueous media. The PIC was prepared easily (50 g), and can be used directly with Pd(OAc)₂ for Suzuki–Miyaura reaction.

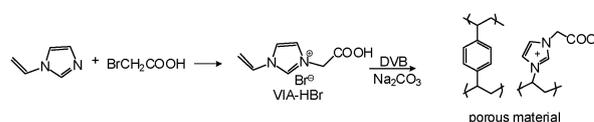
The PIC was prepared as shown in Scheme 1, and the IL (VIA-HBr) was prepared by reaction of 1-vinylimidazole and bromoacetic acid. And VIA-HBr was then copolymerized with DVB in ethanol using azobisisobutyronitrile (AIBN) as the initiator. The copolymer was then treated with Na₂CO₃ to remove HBr to give the ionic copolymer PIC. The detailed experimental section was added as ESI.†

The PIC was characterized by thermogravimetric analysis (see Fig. S1 in ESI†) to detect its thermal stability. The small weight loss before 250 °C resulted from the loss of the adsorbed water. The PIC was stable until 390 °C and the further weight loss above 390 °C was attributed to the decomposition of the PIC. The SEM image showed (Fig. 1) that the material has a sponge-cake structure. On the basis of

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Scheme 1 Preparation of the porous ionic copolymer.

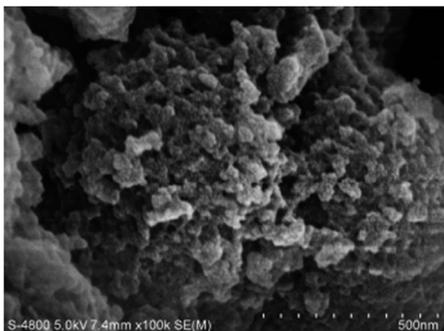


Fig. 1 The SEM image of the PIC.

the nitrogen adsorption–desorption analysis, the BET surface area of PIC was $397 \text{ m}^2 \text{ g}^{-1}$ (Fig. S3 in ESI†) after vacuum pretreatment at $300 \text{ }^\circ\text{C}$, which indicated that the PIC was a stable porous material. The PIC was found to be an irregular porous material with macropores, mesopores and micropores, and BJH analysis gave a total pore volume of 0.29 mL g^{-1} . Large surface and large pore volume of the PIC are highly beneficial to the reactions in catalytic studies.

The catalyst system can be prepared by supporting $\text{Pd}(\text{OAc})_2$ on the PIC directly. Briefly, the Pd catalyst was prepared as follows. The PIC was immersed into $\text{Pd}(\text{OAc})_2$ solution in acetone, and then acetone was removed by evaporation to give the Pd catalyst $\text{Pd}(\text{OAc})_2/\text{PIC}$ (see ESI†). The Pd/PIC nanocatalyst was formed *in situ* in the reaction mixture (Pd catalyzed coupling reaction of 4-bromoanisole with phenylboronic acid under air in water) with $\text{Pd}(\text{OAc})_2/\text{PIC}$, and the $\text{Pd}(\text{OAc})_2$ presumably reduced by phenylboronic acid in the reaction mixture.^{6,13} Pd/PIC can be separated easily by filtration after one cycle of the reaction, and the Pd/PIC nanocatalyst was recyclable (see Fig. S6, S7 and S8 in ESI†) without loss of efficiency. The TEM image of the catalyst after 5 times reaction (Fig. 2, right) indicates that the mean diameter of the nanoparticles is around 2–5 nm, which is similar to the catalyst separated from the reaction mixture firstly (Fig. 2, left). After removing the Pd/PIC nanocatalyst by filtration, no Pd was detected in the filtrate analyzed by ICP-OES (below the detection limitation 7 ppb) and the reaction did not proceed any more in the filtrate, which showed that $\text{Pd}(\text{OAc})_2/\text{PIC}$ was turned into a heterogeneous catalyst after one reaction cycle.

The coupling of 4-bromoanisole with phenylboronic acid was performed as the model reaction with $\text{Pd}(\text{OAc})_2/\text{PIC}$ in water. As shown in Table 1, high yield of 4-methoxybiphenyl was obtained in water under air or argon and the addition of

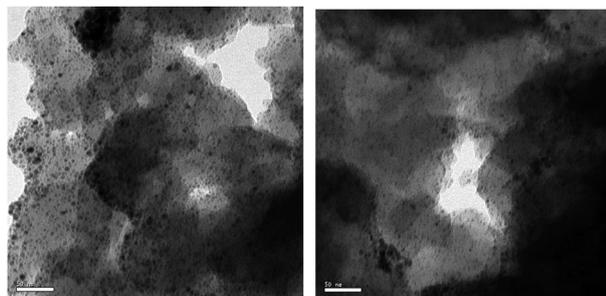


Fig. 2 TEM images of Pd/PIC after 1 reaction cycle (left, scale bar 50 nm); Pd/PIC after 5 reaction cycles (right, scale bar 50 nm).

Table 1 Pd catalyzed Suzuki coupling of 4-bromoanisole with phenylboronic acid^a

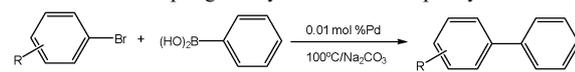
Entry	Time/h	Base	[Pd] (mol%)	Yield ^b (%)
1 ^{c,d}	16	NaOH	1	62
2 ^c	16	NaOH	1	99
3	16	NaOH	1	99
4 ^e	16	NaOH	1	87
5	16	NaOH	0.1	99
6	2	NaOH	0.1	99
7 ^f	2	NaOH	0.01	99
8 ^f	2	Na_2CO_3	0.01	99
9 ^g	40	NaOH	0.001	95

^a Reaction conditions: 4-bromoanisole, 0.5 mmol; phenylboronic acid, 0.75 mmol; base, 1.0 mmol; water, 1 mL; TBAB, 1.0 equiv.; Pd catalyst, 1.0 mol%; under air. ^b Yields were determined by GC analysis, hexadecane used as internal standard. ^c Under argon. ^d Without TBAB. ^e $80 \text{ }^\circ\text{C}$. ^f 4-Bromoanisole, 2.5 mmol; phenylboronic acid, 3.0 mmol; base, 5.0 mmol, H_2O , 5 mL. ^g 4-Bromoanisole, 7.5 mmol; phenylboronic acid, 9.0 mmol; base, 15.0 mmol; H_2O , 15 mL. TBAB = tetrabutylammonium bromide.

the phase transfer agent TBAB enhanced the yield significantly (Table 1, entries 1–3). Since TBAB was a well known stabilizer for nanoparticles, the TBAB presumably played a role also for the stabilization of the Pd nanocatalyst. Interestingly, the coupling reaction of 4-bromoanisole with phenylboronic acid gave 4-methoxybiphenyl in 99% yield with 0.1 mol% or 0.01 mol% loading of Pd in 2 hours (Table 1, entries 4–7). And even with 10 ppm (0.001 mol%) loading of Pd, high yield (95%) was obtained, which showed extremely high activity of the Pd catalyst system (with low Pd loadings, the reaction was scaled up to 2.5–7.5 mmol of 4-bromoanisole) (Table 1, entry 9). A weak base (Na_2CO_3) was also suitable for the reaction and the yield was nearly the same as NaOH used (Table 1, entry 8). It is noteworthy that the products were separated by simple organic extraction and purified by crystallization or by column.

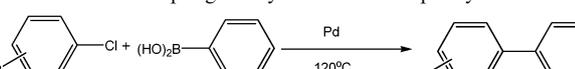
Next, several aryl bromides were coupled with phenylboronic acid with 0.01 mol% Pd loading ($\text{Pd}(\text{OAc})_2/\text{PIC}$) under the optimized reaction conditions. To improve the functional group tolerance, Na_2CO_3 was used as the base. As shown in Table 2, the catalyst showed high efficiency and good functional group tolerance. The coupling reactions of all the aryl bromides with phenylboronic acid proceeded in excellent yields with low Pd loadings (0.01 mol% Pd in most cases). Functional groups, including methoxyl, nitriles, nitro, aldehydes and ketones, were well tolerated under the reaction conditions, and the corresponding products were obtained in high yields (Table 2, entries 1–8, and 11–15). The coupling of 1-naphthyl and 2-naphthyl bromides gave corresponding products in high yields also (Table 2, entries 9 and 10), and *ortho*-substituents in the aryl bromides did not hinder the coupling reactions (Table 2, entries 2, and 12–15).

Afterwards, several aryl chlorides were tested also for the coupling reaction (Table 3). The coupling reaction of electron-poor aryl chlorides afforded the corresponding biphenyl compounds in excellent yields at $120 \text{ }^\circ\text{C}$ in 10 hours with 0.01 mol% to 1% Pd loadings (Table 3, entries 1–3, and 5–8). The deactivated aryl chloride, 4-chloroanisole, was also

Table 2 Suzuki coupling of aryl bromides and phenylboronic acid^a


Entry	R	Yield ^b (%)
1	4-MeO	99
2	2-MeO	98
3	4- <i>tert</i> -Butyl	97
4	4-HCO	97
5	4-MeCO	99
6	4-CN	98
7	4-Me	97
8	4-NO ₂	97
9	1-Naphthyl	95
10	2-Naphthyl	97
11	3-Me	97
12	2-CN	96
13	2-HCO	97
14 ^c	2-Me-5-NO ₂	94
15	2-Me-4-NO ₂	99

^a Reaction conditions: aryl bromides, 2.5 mmol; phenylboronic acid, 3.0 mmol; [Pd] catalyst (Pd(OAc)₂/PIC), 0.01 mol%; Na₂CO₃, 5.0 mmol; TBAB, 2.5 mmol; H₂O, 5 mL; at 100 °C; 2 h; under air. ^b Isolated yield. ^c [Pd] catalyst (0.1 mol%).

Table 3 Suzuki coupling of aryl chlorides and phenylboronic acid^a


Entry	R	Yield ^b (%)
1	4-HCO	93 (95)
2 ^c	4-CN	96 (97)
3 ^d	4-NO ₂	95 (97)
4 ^e	4-MeO	85 (87)
5 ^c	2-CN	93 (95)
6	2-HCO	92 (93)
7	4-MeCO	95 (96)
8 ^{c,f}	4-MeOOC	96

^a Reaction conditions: aryl chlorides, 0.5 mmol; phenylboronic acid, 0.6 mmol; [Pd] catalyst (Pd(OAc)₂/PIC), 1.0 mol%; NaOH, 1.0 mmol; TBAB, 0.5 mmol; H₂O, 1.0 mL; at 120 °C, 10 h under air. ^b Isolated yields (GC yields in parenthesis, hexadecane used as internal standard). ^c Na₂CO₃, 1.0 mmol. ^d [Pd] catalyst, 0.01 mol%. ^e [Pd] catalyst, 3.0 mol%; KOH used instead of NaOH, 1.0 mmol. ^f [Pd] catalyst, 0.1 mol%.

coupled with phenylboronic acid in good yield but with higher Pd loading (Table 3, entry 4). The protocol was widely applicable, and aryl chlorides with functional groups, including methoxyl, nitriles, nitro, aldehydes, ketones and ester groups, were coupled with phenylboronic acid smoothly to obtain corresponding biphenyl compounds.

The PIC has an IL structure (vinylimidazoliumylacetate) with a potential carbene group and a carboxylic group, which is important for the formation and stabilization of Pd nanoparticles. The catalytic activity of Pd is highly dependent on the size of the Pd nanoparticles, and the PIC stabilized the Pd nanoparticles well in about 2–5 nm. Benefited from the use of the PIC for Suzuki–Miyaura reaction, no aggregation of Pd nanoparticles was observed during the reaction and no leaching of Pd occurred on separation of the heterogeneous nanocatalyst. In addition, the PIC material was porous, which was highly profitable for the heterogeneous catalysis.

In summary, we demonstrated a new type of organic porous materials (PIC) by copolymerization of an IL structure with DVB. Application of the PIC was performed as an example and the Pd nanocatalyst was prepared and employed as a highly efficient catalyst for Suzuki–Miyaura reaction. The Pd nanocatalyst (Pd/PIC) was formed *in situ* with Pd(OAc)₂/PIC with a diameter of mainly around 2–5 nm in the Suzuki–Miyaura reaction. Pd/PIC was a heterogeneous catalyst for the coupling reaction with high activity and excellent recyclability. Moreover, Pd/PIC was widely applicable for the coupling reaction of aryl bromides and chlorides, and functional groups, such as methoxyl, nitriles, nitro, aldehydes, ketones and ester groups, were well tolerated under the reaction conditions.

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