



Effective Suzuki coupling reaction enabled by palladium–polycarbene catalyst derived from porous polyimidazolium

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Abstract

N-heterocyclic-carbene based polymers with abundant active sites and excellent stability are fascinating and highly desired while remain rare for the lack of easy synthetic protocols. In this article, an unprecedented strategy that employed a porous polyimidazolium (IPF-CSU-4) as the support for Pd(II) coordination was proposed to develop efficient heterogeneous catalyst. IPF-CSU-4 was constructed via a one-step quaternization chemistry between 2,4,6-tris(1-imidazolyl)-1,3,5-triazine and 1,4-bis(chloromethyl)benzene. The in-situ complexation of palladium (Pd) with carbene ligand of the polyimidazolium readily afforded a Pd-loaded porous polymeric network (Pd-PPc-4) with high stability. Pd-PPc-4 showed favorable accessibility to seven aryl halides substrates in Suzuki coupling reactions, with a catalytic yield up to 99% under mild conditions (3 h, 60 °C) and no obvious loss of activity even after five catalytic cycles. This provides new pathways for developing highly-efficient and stable catalysts through porous organic polymers for typical organic transformations.

Keywords Porous organic polymers · Polyimidazolium · Carbene · Suzuki coupling

1 Introduction

Palladium (Pd)-catalyzed Suzuki coupling reaction has attracted extensive interest as an essential route to construct covalent C–C linkage in modern chemical transformations because of the strong substrate adaptability and functional group tolerance [1, 2]. Recently, numerous efforts have been focused on developing catalysts and optimizing their performance for this C–C coupling strategy. For instance, homogeneous catalysts based on selected ligands such as phosphine ligand [3, 4], *N*-heterocyclic carbenes [5], and bipyridyl ligands [6] have been intensively exploited. The formed Pd complexes through coordination between Pd and the ligand have exhibited promising efficiency for catalyzing Suzuki coupling reactions. Nevertheless, most of the them are expensive and suffer from tedious synthetic procedures, complicated separation as well as poor recyclability, which

still needs to be improved [7, 8]. Additionally, Pd leaching during catalytic cycling process may lead to rapid deactivation of catalysts and inevitable metal contaminations in the product, causing environmental concerns.

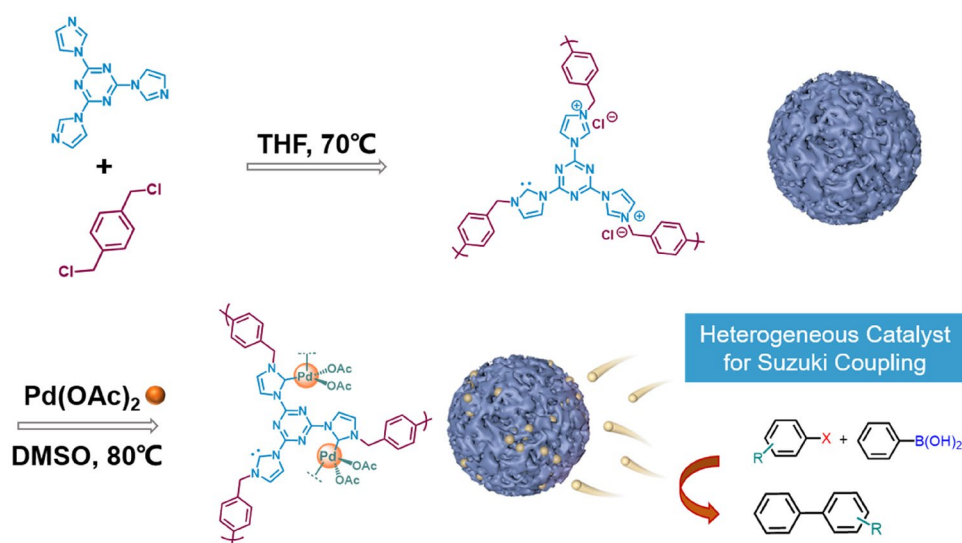
The major advantage of palladium-based heterogeneous catalysts is the recyclability that satisfy wide applications in both academia and industry. Developing efficient heterogeneous analogues by immobilizing palladium complexes or nanoparticles on specific supports, such as silica [9], alumina [10], zeolite [11], and organic polymers [12] turns out to be feasible and promising. Among those numerous and popular supports, organic polymers can easily be prepared by conventional methods, which make them more attractive materials for heterogeneous catalyst supports [13–17]. Ding and coworkers developed an efficient heterogeneous catalytic system (Pd/COF-LZU1) by coordinating Pd moiety onto imine-based covalent organic frameworks and demonstrated its good potentials in Suzuki–Miyaura coupling reaction [18]. Qian et al. described the synthesis of a palladium complex loaded thiadiazole-containing POP (Pd@DTE). They suggested that the strong anchoring group (thiadiazole) contributed to the encapsulation of active species inside the cavities, which endowed Pd@DTE with high stability over multiple catalytic cycles [19]. Wang et al. reported an in-situ formed Pd catalyst on solid and porous polyphenylene

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Scheme 1 Synthetic route of IPF-CSU-4 and Pd-PPc-4



support (Pd/Pphen). The catalyst was synthesized by palladium-catalyzed Suzuki coupling, which directly leads to palladium nanoparticles confined in the polyphenylene network. Pd/Pphen is in turn highly active for further Suzuki coupling reactions, and the performance for non-activated substrates is even superior to the reported molecular catalysts [20]. However, it is still a grand challenge to develop heterogeneous catalysts with easy metal loading methodology and great stability to prevent metal leaking from supports during the catalytic process.

Economic preparation strategy for the support and strong metal-support interactions remain high significant when developing stable matrix-supported Pd heterogeneous catalysts. Introducing *N*-heterocyclic carbenes (NHCs) groups into POP appears to be crucial for addressing some key issues, including preventing the aggregation of metal centers and unexpected metal leaking during catalytic reaction process. Metal aggregation is probably due to the uneven distribution of metal catalytic centers, while metal leaking would be ascribed to the weak electrostatic force between supports and metals [21]. NHCs have unique stabilization and remarkable similarity to electron-rich phosphine ligands in terms of their metal coordination chemistry, which can build a strong coordination bond with metal [22–26]. Recently, several examples of NHC-based porous organic polymers have been discovered and employed as platforms to build heterogeneous catalysts [27–30]. Troschke et al. described the immobilization of a charged imidazolium moiety into a microporous covalent triazine framework (imid-CTF) [30]. The imid-CTF provides intact imidazolium functionalities through a finely adjusted synthetic protocol, as was verified in carbene-catalyzed umpolung reactions.

With the continuous interests to develop easily available and stable heterogeneous catalysts for Suzuki coupling transformation, herein we reported a convenient synthesis of a

porous polyimadazolium and its facile in-situ complexation with Pd(II) (Pd-PPc-4) through *N*-heterocyclic polycarbene. The as-made Pd-PPc-4 exhibited high catalytic performance in comparison with the previously reported homogeneous catalysts, showing no metal leaking in the Suzuki coupling reaction of seven typical aryl halides. This catalyst may be viewed as an alternative to Pd/C and other known heterogeneous Pd-based catalysts.

2 Results and discussion

The porous polyimadazolium, simplified as IPF-CSU-4 (Scheme 1), was prepared through a simple and feasible crosslinking reaction based on the quaternization chemistry of 2,4,6-tris(1-imidazolyl)-1,3,5-triazine (TimTz). The starting TimTz was isolated as a pale yellow powder with a good yield through the nucleophilic substitution of 1,3,5-trichloro-2,4,6-triazine and imidazole (Fig. S1), and its structure was confirmed through classic spectroscopic characterizations (Fig. S2). This chemistry is also in good agreement with the observations [31]. The quaternization between TimTz and 1,4-bis(chloromethyl)benzene was promoted smoothly in tetrahydrofuran under nitrogen at 70 °C, leading to a polyimadazolium. Note that due to the strong electron-withdraw ability of *s*-triazine nuclei a portion of the generated imidazolium rings were reduced by Cl[−] into a radical neutral radical state, which were stabilized by the conjugated π system [32]. After completed polymerizations, the resultant polymer IPF-CSU-4 was subsequently mixed with palladium acetate at 80 °C for 3 h to afford Pd-PPc-4 as a brown-colored powder (85% yield). The as-made Pd-PPc-4 was insoluble in common organic solvents (such as water, tetrahydrofuran, and *N,N*-dimethylformamide) probably due

to its crosslinked nature. The Pd content was recorded to be 32 wt% in Pd-PPc-4 catalyst as determined by ICP.

Fourier transform infrared (FT-IR) spectroscopy of IPF-CSU-4 and Pd-PPc-4 are shown in Fig. 1a. The elimination of absorption peak at 850 cm^{-1} , associated with C–Cl bond, indicates that the complete quaternization of triimidazolium triazine and 1,4-bis(chloromethyl)benzene under our selected experimental conditions. Signals at 1592, 1452 and 1326 cm^{-1} for C=N and C–N proves the successful incorporation of triazine moieties onto the polymer chains. Meanwhile, the characteristic peak at 1702 cm^{-1} for the $\text{N}^+\text{--C}$ ion bond disappeared in Pd-PPc-4, validating the effective coordination between palladium acetate and N-heterocyclic carbenes. Noted that the IPF-CSU-4 sample obtained at $70\text{ }^\circ\text{C}$ give a nearly-identical FT-IR spectrum to those obtained at $120\text{ }^\circ\text{C}$, $150\text{ }^\circ\text{C}$, or $180\text{ }^\circ\text{C}$ (Fig. S3). It suggested the complete polymerization successfully even carried out under the lowest temperature of $70\text{ }^\circ\text{C}$. This would be benefitted from the good activity of the starting materials as well as high efficiency of such quaternization technology. More powerful

evidence was provided by the solid-state ^{13}C NMR (Fig. 1b). The broad chemical shifts in 135, 131 and 122 ppm are corresponding to the carbon atoms on aromatic and imidazole rings. The signal at near 52 ppm is assigned to the carbon atom in methylene, and that at 160 ppm is associated with the carbon atom of the triazine nuclei. After palladium loading, the peak originally appeared at 160 ppm shifted to 163 ppm at a lower field, and the corresponding resonance peaks at 160 ppm was significantly weakened, identifying a high content of Pd-loading through N-heterocyclic carbene ligands. The minor peak at $\sim 36\text{ ppm}$ can be assigned to methyl groups of the residual $\text{Pd}(\text{OAc})_2$ [18].

X-ray photoelectron spectroscopy (XPS) was performed to probe the incorporation of palladium within Pd-PPc-4 (Fig. 1c). The signal at a binding energy (BE) of 337.84 eV corresponds to the $\text{Pd}_{3d_{5/2}}$ in Pd-PPc-4, suggesting the presence of the +2 state Pd species [33, 34]. On the other hand, the BE of 337.84 eV for the Pd(II) species in Pd-PPc-4 shifted negatively by 0.56 eV in comparison with that of 338.4 eV for free $\text{Pd}(\text{OAc})_2$ [18]. This negative shift proves

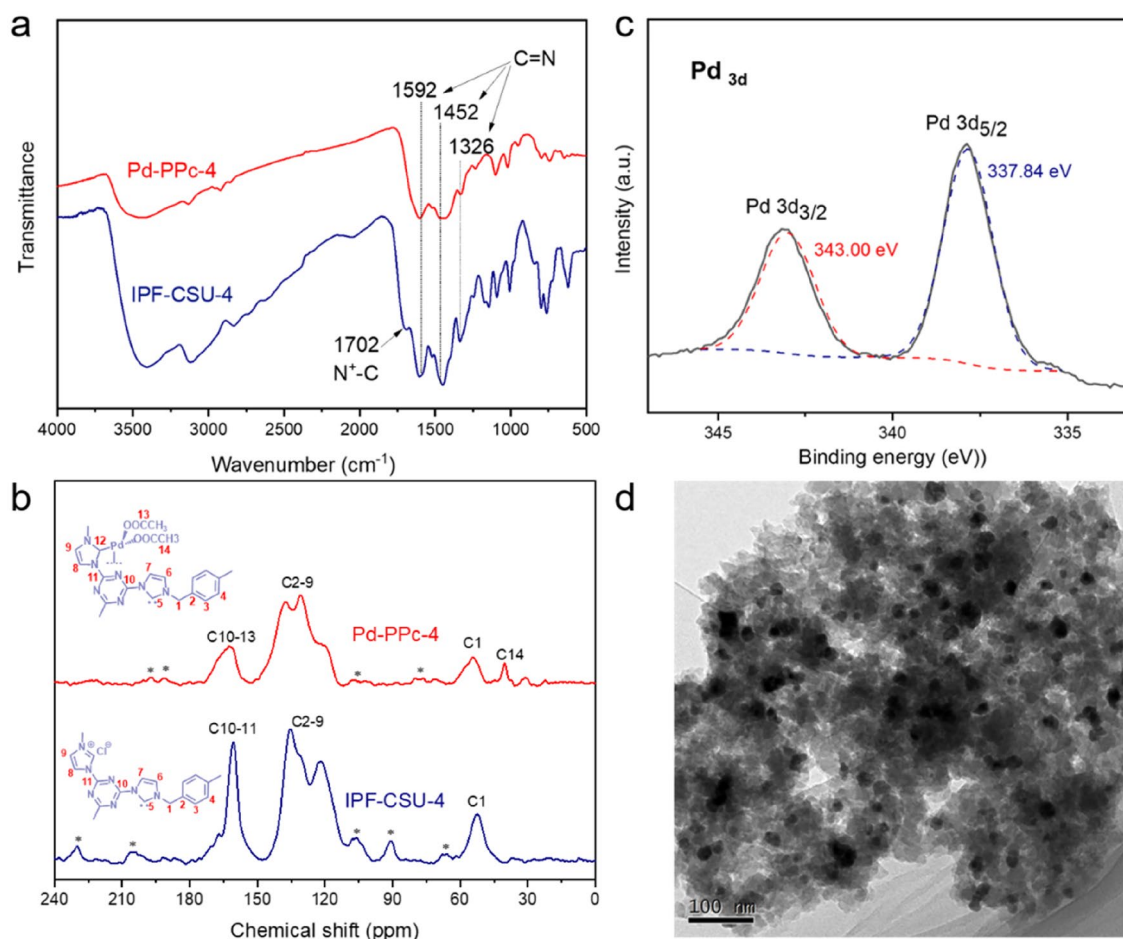


Fig. 1 **a** FT-IR spectra and **b** ^{13}C CP/MAS NMR spectra of Pd-PPc-4 (Red) and IPF-CSU-4 (Blue); **c** X-ray photoelectron spectroscopy and **d** TEM image of Pd-PPc-4 (Color figure online)

the strong coordination of Pd(II) with NHC moieties: the NHC groups further donate electrons to Pd(II) which makes the Pd species less electron-deficient [35].

Scanning electron microscopy (SEM) image of IPF-CSU-4 (Fig. S4a) reveal to relatively uniform spherical particles with a diameter of 3 μm (Fig. S4b). Transmission electron microscopy (TEM) of Pd-PPc-4 show its mesoporosity and the evenly immobilized Pd(OAc)₂ on the pore surface (Fig. 1d), which is well consistent with the SEM analysis. The surface area of IPF-CSU-4 and Pd-PPc-4 were calculated to be 22 and 28 m^2/g respectively. The unsatisfactory surface areas are probably attributed to the high ionic content of polymeric networks as well as many inaccessible micropores when using N₂ probe. Interestingly, the trend of slight increase in surface areas after Pd immobilization is contrary to most other analogues, whose surface areas and pore volumes are considerably reduced on Pd loading as a result of the dispersion of Pd on the pore surface and some pore blocking [36, 37]. We speculate that this difference in porosity is owing to the fact that the metal can combine with multiple carbene groups at the same time, resulting in the increasing crosslinking degree of the polymer [38]. Both the pore size of IPF-CSU-4 and Pd-PPc-4 are mainly distributed in the mesoporous range, with the pore width centering around 2.5 and 3.5 nm for IPF-CSU-4, and 2.7 nm for Pd-PPc-4, respectively, as calculated by Barrett–Joyner–Halenda (BJH) model (Fig. 2b). Except using N₂ as a probe for adsorption–desorption study, CH₄ and CO₂ were also applied as probes to investigate their pore structures, as shown in Fig. S6. Both IPF-CSU-4 and Pd-PPc-4 possess the ability to adsorb these two molecules to some degree as well.

Given the porosity and high content of Pd loading of Pd-PPc-4, Suzuki coupling reaction was conducted as a model reaction to evaluate its feasibility as a heterogeneous catalyst. Iodobenzene and phenylboronic acid were employed as substrates to screen the impact of solvent and base on the catalytic performance (Table S2) [39]. Previous studies have proven that the activity of the coupling reaction can increase to different degrees while adopting the polar organic solvent/water mixed solvent. That is owing to the better solubility of the inorganic base in water, which shortens the catalytic period and thus improves the catalytic activity [39]. Meanwhile, appropriate base can interact with arylboronic acid to form a nucleophilic anion, which is conducive to the metal transfer process. Under the optimized conditions, the targeted product was obtained in a high yield of 99% with K₂CO₃ as a base in a mixed solvent of DMF and H₂O (1:1) for 3 h at 60 °C. This performance was also compared with other heterogeneous and homogeneous catalysts under the same conditions and a comparison were depicted in Table 1. Our Pd-PPc-4 catalytic system is superior to many other POPs supported Pd catalysts, as our system could work well even under milder conditions (Entry 2–4). Of course, other NHC-based heterogeneous catalysts show excellent catalytic effects (Entry 5–7). Compared to many homogeneous catalysts based on palladium-ligand complexes (Entry 8–10), the superior catalytic efficiency of Pd-PPc-4 indicates that IPF-CSU-4 as a support is conducive to the improvement of catalytic performance. We speculate that the ionic polymeric supports and metals are bound by strong coordination bonds, leading to evenly distributed metals on supports and sufficiently accessible catalytic

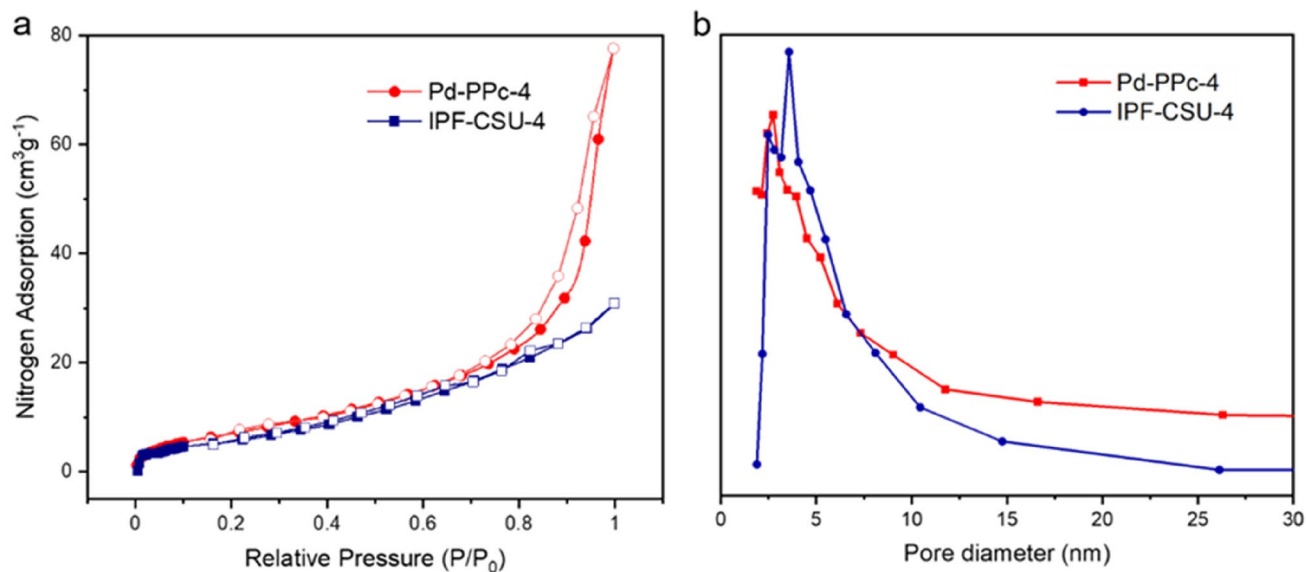
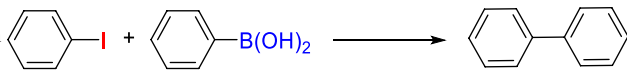
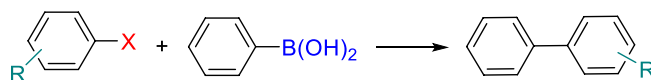


Fig. 2 a N₂ adsorption isotherms and b pore size distribution of IPF-CSU-4 and Pd-PPc-4

Table 1 Comparison of different catalysts for Suzuki coupling reaction


Entry	Catalyst	Surface area (m ² g ⁻¹)	Temperature/time	Yield (%)	Reference
1	Pd-PPc-4 (3 mol%)	28	60 °C/3 h	99	this work
2	P[5]-OCP (0.5 mol% Pd)	–	80 °C/3 h	100	[41]
3	MsMOP-1 (0.47 mmol%)	554	80 °C/1 h	99	[42]
4	Pd/COF-LZU1 (0.5 mol%)	146	150 °C/3 h	97	[18]
5	Poly-NHC-2–Pd ²⁺ (0.057 mol%)	569	80 °C/1 h	99	[43]
6	Fe ₃ O ₄ @SiO ₂ @NHC@Pd–MNPs (0.00394 mmol%Pd)	–	80 °C/5 min	99	[44]
7	Ru–CP–Pd (0.1 mol%)	–	90 °C/8 h	98	[45]
8	Pd[P(C ₆ H ₅) ₃] ₄	–	60 °C/3 h	82	This work
9	Pd(OAc) ₂	–	60 °C/3 h	63	This work
10	[(C ₆ H ₅) ₃ P] ₂ PdCl ₂	–	60 °C/3 h	9	This work
11	IPF-CSU-4	22	60 °C/3 h	0	This work

Reaction conditions: iodobenzene, 1 mmol; phenylboronic acid, 1.3 mmol; catalyst, 10 mg; K₂CO₃, 1 mmol; DMF/H₂O=1:1(4 ml); at 60 °C; 3 h; under N₂

Table 2 Suzuki coupling reaction with different reaction substrates

Entry	R	X	Yield (%)
1	H	I	99
2	4-OH	I	89
3	4-OCH ₃	I	79
4	H	Br	68
5	4-OH	Br	64
6	4-NH ₂	Br	46
7	4-OCH ₃	Br	39

Reaction conditions: aryl halide, 1 mmol; phenylboronic acid, 1.3 mmol; Pd-PPc-4 catalyst, 10 mg; K₂CO₃, 1 mmol; DMF/H₂O=1:1 (4 ml); at 60 °C; 3 h; under N₂

sites [40]. The reaction with metal-free ionic polymer precursor IPF-CSU-4 as the catalyst, however, gave no product (Entry 10), demonstrating the significant role of palladium in the catalytic process.

To estimate the generality of this Pd-PPc-4 system as a heterogeneous catalyst, the Suzuki coupling reaction of seven aryl halides with phenylboronic acid was conducted. It readily afforded the corresponding biaryls under the optimal conditions of 60 °C and 3 h (Table 2). Apparently, when the reaction group is iodine atom, the yield is better than that of bromine atom (Entry 1 and 5). This would be explained by the superior reactivity of iodobenzene [45, 46]. Similarly, the conclusion also stands in the cases of substances

with electron-withdrawing/donating groups (Entry 2 and 5 or Entry 3 and 7). The electron-donating substituents on aryl halides usually have more negative effect compared with electron-withdrawing ones. It would be reasonable considering the fact that the electron-withdrawing substituents usually lead to the activation of the C–X bond [47].

A possible catalytic mechanism of Pd-PPc-4 for Suzuki coupling reaction was proposed (Fig. S8). It is well consistent with other known heterogeneous systems [4]. Pd-PPc-4 system gave a typical heterogeneous manner. Investigation on recyclability reveals that the catalyst is highly stable and can be filtered and reused in a new coupling reaction up to 5 times without substantial loss of its activity (Fig. 3a).

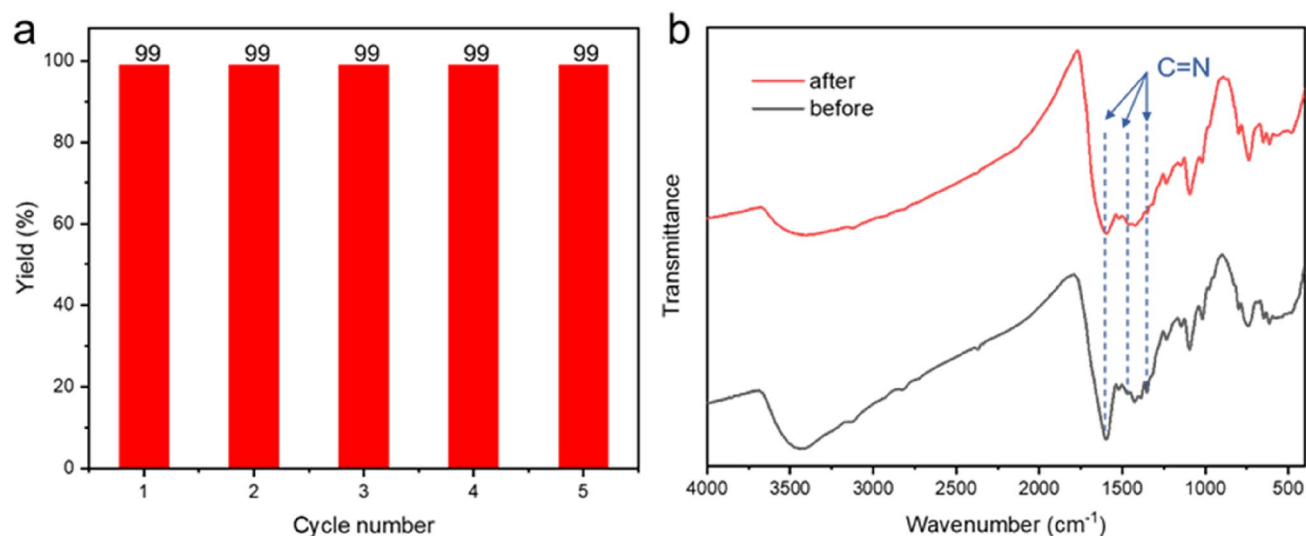


Fig. 3 **a** Reusability of the Pd-PPc-4 catalyst in Suzuki coupling reactions and **b** partial FT-IR spectra for Pd-PPc-4 before and after reused five times

Meanwhile, the structural feature of the catalyst was retained after the catalytic cycles, as identified by FT-IR spectroscopic monition (Fig. 3b). Additionally, a hot-filtration test was carried out in the Suzuki coupling reaction of iodobenzene with phenylboronic acid at 60 °C. Pd-PPc-4 was filtered out from the reaction mixture after the catalytic reaction was carried out for 2 h, and the reaction was kept for a further 2 h. The catalytic yield remained almost no changes before and after filtration. We found that Pd species is completely absent in the solution and the supernatant shows no catalytic activity. These results suggest almost negligible degree of metal leaking during this catalytic process. The good stability of our catalytic system may result from the reduced metal aggregation and strong coordination bond between the metal and support.

3 Conclusions

In summary, we report an easy-to-handle and scalable strategy for developing porous organic polymer-based palladium catalyst based on a porous polyimidazolium support. The as-made Pd–polycarbene catalytic system worked well in Suzuki coupling reaction. Compared with small molecule catalysts, the heterogeneous catalyst showed superior catalytic activity with wide substrate adaptability even under milder reaction conditions. Additionally, exceptionally high recyclability was demonstrated, benefiting from the strong coordination bond between metal and polycarbene. However, the development of Pd-PPc-4 catalyst still needs further efforts, including decreasing metal content without damaging the catalytic efficiency, reducing catalyst size and

increasing TOF value. In addition, optimization of porous polymer support including cross-linking degree, porosity, ionic salt activation ability also deserves more research. This study indicates a promising aspect of porous ionic polymers and highly-efficient and stable Pd–polycarbene heterogeneous catalysts for organic transformations into value-added products in an environmental-friendly manner.

Appendix: Supplementary data

Synthetic route of 2,4,6-tris(1-imidazolyl)-1,3,5-triazine (Fig. S1), (a) ^1H NMR spectrum; (b) ^{13}C NMR spectrum; and (c) FT-IR spectrum of triimidazolyl triazine (Fig. S2), FT-IR spectra of IPF-CSU-4 obtained at 70°C, 120°C, 150°C, and 180°C (Fig. S3), SEM spectroscopy of (a) IPF-CSU-4 and (b) Pd-PPc-4 (Fig. S4), TEM spectroscopy of Pd-PPc-4 (Fig. S5), (a) CH_4 and (b) CO_2 adsorption/desorption isotherms of IPF-CSU-4 and Pd-PPc-4 (Fig. S6), Mass spectrum of IPF-CSU-4 (Fig. S7), Proposed mechanism of Suzuki reaction catalyzed by Pd-PPc-4 (Fig. S8), Pore parameters of the polymers IPF-CSU-4 and Pd-PPc-4 (Table S1), Catalytic condition optimization of Suzuki coupling reaction (Table S2), ^1H NMR spectrum of catalytic products (Figs. S9–11).

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10934-021-01193-y>.

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Declarations

Conflict of interest We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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