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Urea-based amphiphilic porous organic polymer-supported palladium as a reusable catalyst for Suzuki–Miyaura coupling and hydroxycarbonylation reactions in water

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The development of environmentally friendly heterogeneous catalysts for organic reactions in water is becoming of growing importance for the development of sustainable processes. In this work, a porous organic polymer-supported palladium catalyst (Pd@UPOP-1) was successfully fabricated from 3,3'-diaminobenzidine and methylenediphenyl diisocyanate through a facile urea-forming condensation reaction. The structure and composition of the catalyst were characterized using several physicochemical methods. Pd@UPOP-1 was found to possess good porous structure and excellent amphiphilicity. Under mild reaction conditions, the catalyst showed excellent catalytic activity and good substrate compatibility for the Suzuki–Miyaura coupling reaction of aryl bromides, as well as the hydroxycarbonylation reaction of aryl iodides. In addition, the catalyst could be used for several consecutive recycles in both cases.

KEYWORDS

amphiphilicity, carbonylation, palladium, porous organic polymer, water

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1 | **INTRODUCTION**

Water is a cheap, safe and nontoxic solvent and has thus attracted considerable attention when it is used as a solvent in organic synthesis.^[1-3] Meanwhile, the functionalization of aryl halides is of major importance in the field of modern organic chemistry due to the ubiquity of aromatic and heteroaromatic units.^[4-6] However. the catalytic transformations of aryl halides in water generally require water-soluble homogeneous catalysts, which suffer from practical problems such as catalyst separation and recycling.^[3,7–9] In addition, homogeneous systems generally induce contamination of the ligand and metal residue in products.^[10,11] From the standpoint of green and sustainable organic synthesis, environmentally friendly, efficient and recyclable heterogeneous catalysts for transformation reactions of aryl halides in water offer a solution to these vital problems by facilitating product separation and catalyst reuse.^[12-17]

Palladium complexes represent the most powerful catalysts for coupling reactions of aryl halides.^[18] In this regard, great effort has been made to immobilize palladium complexes on various organic and inorganic solid supports to create heterogeneous catalysts,^[19-23] as well as these hydrophilic heterogeneous catalysts being used in aqueous conditions.^[24] Among various catalytic supports, polymers have attracted great attention due to their excellent capability of post-synthetic modification.^[21,22] However, catalysts supported on traditional polymers have basic problems in terms of tedious synthetic routes. fewer and inhomogeneously distributed active sites, low specific surface area, poor stability, as well as low efficiency in mass transport.^[25] Hence, developing more active and heterogeneous catalytic systems is imperative and merits further study.

Porous organic polymers (POPs), which feature high surface areas and designable pore structures, have attracted great attention recently due to their potential to combine the best features of homogeneous catalysts and heterogeneous catalysts.^[25-30] A series of POPs containing various nitrogen ligands and phosphine ligands have been successfully synthesized and used as catalyst supports.^[31-33] Results showed that some of them even exhibited higher catalytic activities than the corresponding homogeneous counterparts. However, the overwhelming majority of POPs mainly consist of hydrophobic aromatic frameworks, which lead to their poor dispersion in water and results in low accessibility towards substrates.^[34,35] Hence, the construction of porous polymers with both porosity and good hydrophilicity still remains to be explored. In 2014, Wang and co-workers^[36] made an important contribution to the preparation of amphiphilic porous polymers by using

the facile urea-forming condensation reaction, though it needs tedious reaction procedures and the use of hypertoxic chemicals.^[36] Very recently, we reported a facile method for the preparation of amphiphilic porous polyurea (UPOP) via the condensation of readily available 3,3'-diaminobenzidine (DAB) and 1,4-phenylene diisocyanate,^[13] and a UPOP-supported palladium catalyst exhibited excellent catalytic activity for aminocarbonylation reactions in water.

In order to explore the generality of the preparation strategy of urea-based amphiphilic polymer and extend the applications of UPOP to different catalytic reactions, in the work reported in this paper, an amphiphilic porous organic polymer-supported palladium (Pd@UPOP-1) catalyst was fabricated via the urea-forming condensation of DAB and methylenediphenyl diisocyanate (MDI), followed by immobilization of palladium acetate (Scheme 1). The catalytic performances of Pd@UPOP-1 were evaluated for the Suzuki–Miyaura coupling and hydroxycarbonylation reactions of aryl halides in water.

2 | EXPERIMENTAL

2.1 | Materials

DAB (99%) and MDI (98%) were obtained from Meryer Chemical Technology (Shanghai) Co. Ltd, and used as received. Palladium acetate (99%) was purchased from Energy Chemical (Shanghai) Co. Ltd. Aryl halides, arylboronic acids and bases were of analytical reagent grade. 1,4-Dioxane was an analytical reagent and purified by refluxing over sodium. CO with a purity of 99.99% was purchased from a local manufacturer.

2.2 | Preparation of Porous Polymer

UPOP-1 was prepared according to the synthetic procedure for UPOP with some modifications.^[13] Generally, freshly dehydrated 1,4-dioxane (80 ml) was added to a 250 ml flask, followed by the addition of 2.0 g of MDI (8.0 mmol). After the mixture was heated to 80 °C, a solution of DAB (0.85 g, 4.0 mmol) in 80 ml of 1,4-dioxane was added slowly in an oil bath and then stirred at 80 °C for 4 days. After the reaction, the resulting pale-yellow solid was washed with methanol, tetrahydrofuran and diethyl ether, and dried under vacuum (2.82 g). The prepared polymer was designated as UPOP-1.

2.3 | Preparation of Catalyst

Pd@UPOP-1 was obtained following the same procedures as for the synthesis of Pd@UPOP.^[13] Generally, UPOP-1 (1.0 g) was added to a solution of palladium acetate



SCHEME 1 Synthesis of urea-based amphiphilic polymer-supported palladium catalyst

(0.0443 g) in 30 ml of dichloromethane and stirred at room temperature for 12 h. Pd@UPOP-1 was collected with a Hirsch funnel, washed with acetone, purified by Soxhlet extraction with acetone for 24 h and then dried under vacuum. The palladium content was 1.9 wt% as determined using atomic absorption spectroscopy.

2.4 | Typical Procedure for Suzuki-Miyaura Coupling Reactions

Suzuki–Miyaura coupling reactions were performed under ambient conditions in a 10 ml reaction flask. Generally, Pd@UPOP-1 containing 1 mol% Pd, aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol), base (1.0 mmol) and water (4 ml) were loaded into the flask. Then, the flask was stirred at 25 °C until aryl bromide was totally consumed (determined by TLC). For the coupling reactions of aryl chlorides, the reaction was heated at 85 °C for 24 h. After that, the mixture was separated by centrifugation and the catalyst was extracted with copious ethyl acetate. Then, the combined liquid was concentrated and purified by TLC using petroleum ether as eluting solvent. Purity of products was determined using ¹H NMR analysis (Supporting Information) and yields were based on aryl bromides.

2.5 | Typical Procedure for Hydroxycarbonylation Reactions

These catalytic reactions were carried out in a Teflonlined stainless steel autoclave (50 ml) that was equipped with a magnetic stirrer bar and an automatic temperature controller. In a typical experiment, Pd@PUP-1 containing 1 mol% Pd, aryl iodide (1.0 mmol), K₂CO₃ (1.0 mmol) and deionized water (5 ml) were added to the autoclave. After purging four times with CO, the autoclave was pressurized with CO to 5 bar. Then, the reaction was allowed to react at 100 °C for a definite time. The resulting mixture was separated by centrifugation. The solid was extracted with copious methanol and the combined liquid was acidic to litmus with HCl (5 wt%). Then, the liquid was extracted five times with 5 ml of EtOAc. The combined organic layers were dried over MgSO₄ and vacuum-evaporated to afford the products. Purity of products was determined using by ¹H NMR analysis (Supporting Information) and yields were based on aryl iodides.

2.6 | Adsorption of Chlorobenzene

The adsorption capacity of Pd@UPOP-1 for chlorobenzene was determined as follows. Generally, Pd@UPOP (0.3 g) was added to 2.0 g of chlorobenzene in 20 ml of deionized water under magnetic stirring. After stirring at 25 °C for 60 min, the mixture was centrifuged at 5000 rpm for 10 min. The obtained solid was extracted four times with 5 ml of ethanol, and the collected ethanol was then analyzed with gas chromatography.

2.7 | Characterization

Nitrogen sorption isotherms were obtained with a Micrometrics ASAP 2020 system at 77 K, the polymer being pretreated under vacuum at 100 °C for 5 h before the measurements. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The pore size distribution was calculated using the nonlocal density functional theory (NLDFT) method. Fourier transform infrared (FT-IR) spectroscopy was conducted with a Bruker Equinox 55 FT-IR spectrophotometer using the KBr pellet technique, over the range 400–4000 cm^{-1} at a resolution of 2 cm^{-1} . The size and morphology of the polymer was observed with a Hitachi SU8000 field emission scanning electron microscopy (SEM) instrument. X-ray photoelectron spectroscopy (XPS) measurements of the polymer and catalyst were carried out with a VG Multilab 2000 spectrometer using a Mg-Al_{Ka} X-ray source, and the C1s transition was adjusted to 284.8 eV. Thermogravimetric analysis was conducted with a 4 of 9 WILEY-Organometallic

NETZSCH STA 449 F5 instrument under a dynamic nitrogen atmosphere, and the sample was heated from room temperature to 600 °C at a heating rate of 10 °C min⁻¹. ¹H NMR spectra were recorded with a Bruker Avance III NMR spectrometer (400 and 100 MHz) at ambient temperature. The contact angles were measured with a Dataphysics OCA 20 system. Atomic absorption spectroscopy was performed with a PerkinElmer AA-300 spectrophotometer. GC analysis was performed using a ScientificTM TRACETM 1310 apparatus equipped with a TRACE TR-WAX capillary column and a flame ionization detector.

3 | **RESULTS AND DISCUSSION**

3.1 | Characterization of Catalyst

The FT-IR spectra of UPOP-1, Pd@UPOP-1 and reactive monomers are shown in Figure 1. MDI shows a stretching band of isocyanate at 2278 cm⁻¹. While the band at 2278 cm⁻¹ was absent in the spectrum of UPOP-1, and a new stretching band of C=O at 1650 cm⁻¹ emerged. These results suggest that the condensation reaction between DAB and MDI was finished.^[13,36]

XPS studies were performed to investigate the elemental compositions of the surface and coordination states of Pd species. In Figure 2(a), the XPS results for UPOP-1 validated that C, N and O elements were present in the polymer. The XPS spectrum of Pd@UPOP-1 (Figure 2b) revealed that Pd species were present in the Pd²⁺ state, corresponding to a binding energy of 337.7 eV in the Pd $3d_{5/2}$ level. In comparison with that of free Pd (OAc)₂ (338.4 eV),^[37] the Pd²⁺ binding energy in the Pd@UPOP shifted negatively by 0.7 eV, which



FIGURE 1 FT-IR spectra of DAB, MDI, UPOP-1 and Pd@UPOP-1



FIGURE 2 XPS spectra: (a) XPS spectra of UPOP-1 and Pd@UPOP-1 (elemental scan); (b) XPS spectrum of Pd in Pd@UPOP-1

should be attributed to the interaction of Pd $(OAc)_2$ with the UPOP-1 support.

The thermogravimetric analysis of UPOP-1 is depicted in Figure 3. There is no obvious weight loss below 250 °C, and rapid weight loss that takes place at 280–550 °C, suggesting that UPOP-1 can be stable at least up to 250 °C.

Nitrogen adsorption-desorption isotherms and pore size distribution curve of UPOP-1 are shown in Figure 4. The sample exhibits typical sorption behavior of type IV. A sharp rise at medium- and high-pressure regions $(P/P_0 = 0.8-1.0)$ indicates the presence of macropores. The appearance of hysteresis could be an indicator for the softness of UPOP-1, demonstrating the deformation and swelling of the network.^[38] UPOP-1 has a BET surface area of 146 m² g⁻¹. The pore size distribution curve (inset of Figure 4) of UPOP-1 based upon the NLDFT calculation method reveals that the sample has a very broad



FIGURE 3 Thermogravimetric analysis of UPOP-1



FIGURE 4 Nitrogen adsorption (filled symbols)-desorption (open symbols) isotherms and pore size distribution curve of UPOP-1

pore size distribution, suggesting its hierarchical porous structure comprised of micropores and mesopores.

SEM and transmission electron microscopy (TEM) images of UPOP-1 are shown in Figure 5. The images show that that UPOP-1 exhibited a sponge-like three-dimensional network morphology with abundant macroporous structures. Thus, SEM and TEM images provide further evidence of porosity.

Given that hydrophilic urea linkages could impart wettability to UPOP-1, the wettability of Pd@UPOP-1 polymer was thus investigated. The wettability was firstly examined using contact angle measurements. Figure 6 illustrates the contact angles of Pd@UPOP-1 for water and salad oil droplets. The contact angle between Pd@UPOP-1 and water was about 53°, indicating a good hydrophilicity. While for salad oil, the droplet was VILEY Organometallic 5 of 9 Chemistry

quickly absorbed without any residue, and the contact angle was recorded as 0°. The catalyst was also dispersed in water and hexane to further investigate its amphiphilicity (Figure 7). The results show that Pd@UPOP-1 was well dispersible in water and retained in the aqueous phase in a water-hexane biphasic system. These results suggest that the synthesized Pd@UPOP-1 has good amphiphilic property. The hydrophilicity could be ascribed to the hydrophilic urea moieties, and the strong oleophilicity was ascribed to the presence of hydrophobic composition of phenyl rings. Thus, a porous and amphiphilic catalytic support for heterogeneous catalysis was achieved.

3.2 | Suzuki-Miyaura Coupling Reactions

For the purpose of extending the applications of ureabased amphiphilic polymer catalyst, the catalytic performance of Pd@UPOP-1 was initially evaluated for the Suzuki-Miyaura coupling reaction of aryl bromides in pure water. Our study began with the coupling reaction of bromobenzene and phenylboronic acid in the presence of K₂CO₃ as base. After reacting at room temperature for 12 h, 1.0 mol% Pd@UPOP-1 gave a GC yield of biphenyl of 81% with nearly 100% selectivity (Table 1, entry 1). Previous research indicated that bases had significant effects on the activity of the Suzuki-Miyaura coupling reaction.^[39] Hence, several organic and inorganic bases were investigated for this coupling reaction (Table 1, entries 2-6). Among the bases screened, K₂CO₃ was identified as optimal, providing a GC yield of 99% after a prolonged reaction time (Table 1, entry 7). Thus, a highly active catalyst was obtained for the Suzuki-Miyaura coupling reaction. Given the structure and properties of Pd@UPOP-1, its excellent catalytic performance should be attributed to the special amphiphilic porous structure. The good hydrophilicity enabled its effective dispersion in water and good contact with organic substrates, while the porous structure and strong oleophilicity provided a microenvironment with high concentration of organic substrates inside the frameworks. As a proof of high concentration of organic substrates inside the frameworks, an adsorption experiment in water showed that the adsorption capacity of Pd@UPOP-1 for chlorobenzene was 2907 mg g^{-1} , while the solubility of chlorobenzene in water was only 0.4 mg g^{-1} under the same conditions.

With the optimal conditions in hand, we next investigated the scope and generality of this Suzuki–Miyaura coupling reaction (Table 2). Firstly, various aryl bromides were examined using phenylboronic acids as the coupling partners. The results showed that aryl bromides bearing both electron-withdrawing and electron-donating groups participated in the reactions readily, affording the





FIGURE 5 (a, b) SEM and (c, d) TEM images of UPOP-1



FIGURE 6 Images of contact angle measurements for Pd@UPOP-1: (a) photograph of a water droplet; (b) photograph of a salad oil droplet

corresponding biaryl products in good to excellent yields within 30 h (Table 2, entries 1–10). The scope of arylboronic acids for this catalytic Suzuki–Miyaura coupling reaction was also examined. The reactions with various arylboronic acids proceeded smoothly, and excellent yields of biaryls were obtained regardless of the



FIGURE 7 Hydrophilic measurements of Pd@UPOP-1: in water (left); in water-hexane (right)

electronic nature of the aryl boronic acids (Table 2, entries 11–14). Activated aryl chlorides, such as 4-CN-, 4-NO₂- and 4-CF₃-substituted chlorobenzenes, were also investigated under the optimized reaction conditions. Unfortunately, no target biaryls were detected after the reaction. On further elevating the reaction temperature to 85 °C, moderate yields of corresponding biaryls were obtained after 24 h (Table 2, entries 15–17).

In addition to catalytic activity, the recovery and reusability of the catalyst are also crucial in the evaluation of economic feasibility of a catalytic process. To evaluate the recyclability and reusability of the Pd@UPOP-1 catalyst, we performed the Suzuki–Miyaura coupling reaction of

TABLE 1 Effect of catalyst and base^a

Br	+ BOH	$\frac{Pd (1 \text{ mol}\%)}{H_2O, \text{ base}}$	
Entry	Base	Time (h)	Yield (%) ^b
1	K ₂ CO ₃	12	81
2	K ₃ PO ₄	12	64
3	KHCO ₃	12	47
4	КОН	12	54
5	DBU	12	79
6	Et ₃ N	12	77
7	K ₂ CO ₃	18	99

 a Reaction conditions: Pd@UPOP-1 (1.0 mol% Pd), bromobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), base (1 mmol), water (4 ml), 25 °C, stirring speed of 600 rpm.

^bGC yield.

TABLE 2	Suzuki-Miyaura	coupling	reaction	catalyzed	by
Pd@UPOP ^a					

	Pd@UPOP-1 (1 mol%)				
	$+ R_2$	(OH) ₂ H	$\frac{l_2O, K_2CO_3}{RT} \langle $		
	~			$R_1 R_2$	
Entry	R ₁	R ₂	Time (h)	Yield (%) ^b	
1	<i>p</i> -Me	Н	24	94	
2	<i>m</i> -Me	Н	26	99	
3	o-Me	Н	28	97	
4	p-F	Н	24	93	
5	<i>p</i> -OMe	Н	25	92	
6	p-OH	Н	24	99	
7	р-СНО	Н	18	91	
8	<i>p</i> -COMe	Н	16	96	
9	p-CN	Н	15	95	
10	p-C ₆ H ₅	Н	30	98	
11	Н	<i>p</i> -Me	18	97	
12	Н	o-Me	18	97	
13	Н	p-COMe	18	99	
14	Н	p-CN	18	94	
15 ^c	F ₃ C-Cl	Н	24	70	
16 ^c	O ₂ N-	Н	24	87	
17 ^c	NC-	Н	24	65	

^aReaction conditions: Pd@UPOP-1 (1.0 mol% Pd), aryl bromide (1.0 mmol), arylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), water (5 ml), 25 °C, stirring speed of 600 rpm.

^bIsolated yield.

^cAryl chlorides as substrate, reaction temperature was 85 °C.



FIGURE 8 Reuse of Pd@UPOP-1 catalyst for Suzuki–Miyaura cross-coupling reaction. Reaction conditions: Pd@UPOP-1 (1.0 mol% Pd), *p*-bromoanisole (1.0 mmol), phenylboronic acid (1.5 mmol), K₂CO₃ (2.0 mmol), water (5 ml), 25 °C, 25 h, stirring speed of 600 rpm

p-bromoanisole with phenylboronic acid under the optimized reaction conditions. After the completion of the reaction, the reaction mixture was centrifuged and filtered. The recovered Pd@UPOP-1 was washed with methanol and dried under vacuum at 60 °C before use for the next catalytic run. The obtained liquid was analyzed using GC. Figure 8 shows that Pd@UPOP-1 could be effectively used up to four times with a slight decrease of its activity observed. XPS analysis of recovered Pd@UPOP-1 after four recycles (Figure 9) showed the coexistence of Pd(0) and Pd (II) species in the recycled catalyst, and the ratio of Pd⁰/Pd²⁺ is 1.83 as estimated by the proportion of relative peak areas. This suggested that the reduction of Pd²⁺ occurred during the reaction.



FIGURE 9 Pd 3d XPS spectrum of the recovered Pd@UPOP-1

TABLE 3 Hydroxycarbonylation of iodobenzene^a

$I + CO \xrightarrow{(1) \text{Pd@UPOP-1 (1 mol\%)}} OH$				
Entry	Base	Time (h)	Recycle no.	Yield (%) ^b
1	K_2CO_3	5	Fresh	64
2 ^c	КОН	10	Fresh	77
3	K_2CO_3	10	0 (fresh)	90
4	K_2CO_3	10	1	91
5	K ₂ CO ₃	10	2	88
6	K ₂ CO ₃	10	3	89
7	K ₂ CO ₃	12	4	82

^aReaction conditions: Pd catalyst (1.0 mol%), iodobenzene (1.0 mmol), K₂CO₃ (1.0 mmol), water (5 ml), 100 °C, CO (5 atm), stirring speed of 600 rpm.

^bIsolated yield.

^cKOH (2.0 mmol).

TABLE 4 Hydroxycarbonylation of aryl iodides^a

R_1	I + CO (1)	Pd@UPOP-1 (1 mol%) (2) HCl	
Entry	R	Time (h)	Yield (%) ^b
1	<i>p</i> -Me	12	85
2	<i>p</i> -OMe	12	89
3	р-ОН	10	91
4	p-NO ₂	10	87
5	p-Cl	10	87
6	m-Cl	10	84
7	o-Cl	12	85
8	N I	15	37

^aReaction conditions: Pd catalyst (1.0 mol%), aryl iodide (1.0 mmol), K_2CO_3 (1.0 mmol), water (5 ml), 100 °C, CO (5 atm), stirring speed of 600 rpm. ^bIsolated yield.

3.3 | Hydroxycarbonylation Reactions

Benzoic acids are common structural motifs in many natural products, pharmaceuticals and agrochemicals.^[40,41] Palladium-catalyzed hydroxycarbonylation of aryl halides represents a widely used approach for preparing such compounds. The encouraging catalytic performance of Pd@UPOP-1 in Suzuki–Miyaura coupling reactions prompted us to further explore it application in the hydroxycarbonylation of aryl iodides. When the hydroxycarbonylation reaction of iodobenzene was carried out with 1 mol% Pd@UPOP-1 as the catalyst, a yield of 64% of benzoic acid was obtained in 5 h (Table 3, entry 1). Further optimizing the base and reaction time, 1 mol% Pd@UPOP-1 provided a yield of 90% of benzoic acid in 10 h with K_2CO_3 as the base (Table 3, entry 3). After initial experimentation, the reaction mixture was filtered. The recovered Pd@UPOP-1 was washed with sufficient methanol and dried under vacuum. Then, the solid was subjected to the next run of hydroxycarbonylation by charging with the same substrates, base and solvent. The results show that Pd@UPOP-1 could be effectively recycled and reused for up to four consecutive runs.

Various aryl iodides were used to investigate the scope of this catalytic hydroxycarbonylation (Table 4). When the reaction was performed in water at 100 °C for 10–15 h, a variety of aryl iodides could be carbonylated to the corresponding aryl acids in moderate yields. Aryl iodides bearing different functional groups, such as p-CH₃, p-OCH₃, p-OH, p-C, and p-NO₂, were well tolerated, and the electronic nature of substituent groups had no obvious effect on the yields of the reaction (Table 4, entries 1–7). 2-Iodopyridine, as a representative example of an aromatic heterocyclic iodide, afforded the target acid in a yield of 37%.

4 | CONCLUSIONS

An amphiphilic POP-supported palladium catalyst was easily fabricated via a facile urea-forming condensation reaction. Characterization results show that the prepared polymer possesses relatively high surface area, hierarchical porosity and amphiphilicity. Under mild reaction conditions, the catalyst displayed excellent catalytic activities for two types of organic reaction in water: (i) Suzuki-Miyaura coupling of aryl bromides and (ii) hydroxycarbonylation of aryl iodides. The high catalytic performance in water could be attributed to the amphiphilic and porous structure of the catalyst, which could provide a microenvironment with a high concentration of organic substrates inside the frameworks. Furthermore, the catalyst can be easily recovered and reused several times without significant loss of catalytic activity. The result obtained in this study could offer an attractive method and good reference for the development of heterogeneous catalysts in water.

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