

# Palladium catalyst immobilized on functionalized hyper-crosslinked polymers with 8-hydroxyquinoline as monomer for Suzuki-Miyaura coupling reactions

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## Research Article

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# Abstract

An efficient and stable palladium species catalyst immobilized on functionalised hyper-crosslinked polymers (HCPs-Pd) has been successfully developed and applied in the Suzuki-Miyaura coupling reaction of diverse types of aromatic halides with aromatic boric acid in this work. The results demonstrated that HCPs-Pd exhibited high catalytic activity, which benefited from the microporous structure of the catalyst guaranteed high dispersibility of active palladium, and high specific surface area, large pore volume, good chemical stability. Under optimal reaction conditions, 93.0% of biphenyl yield in the Suzuki-Miyaura reaction with bromobenzene ( $C_6H_5Br$ ) and phenylboric acid ( $C_6H_7BO_2$ ) as raw material was obtained. The good stability of the HCPs-Pd catalyst was verified by five cycles experiments. Perhaps this work provides new insights into the high-yield preparation of biphenyl aromatic compounds employing HCPs-Pd as an efficient and stable catalyst in the Suzuki-Miyaura reaction.

## Introduction

As an essential part of the porous organic polymers (POPs), the hyper-crosslinked polymers (HCPs) have been shown to display superior properties, including high surface area ( $S_{BET}$ ) and pore volume, special porosity and easy to prepare and chemical modify. Therefore, they have remarkable potentials for the adsorption materials and catalytic materials [1–4]. Compared with other materials, the diversity of synthesis is the great advantage of HCPs, which can have different structures through connecting different parts [5, 6].

Compared with the material HCPs, the catalytic activity and stability of the immobilized precious metal were significantly improved, because of its organic cage frameworks and the coordination between the heteroatoms in HCPs and metal ions, which could fix the ultra-fine metal nanoparticles in the cages and make the metal particles firmly anchored to maintain an excellent activity in the long term, as well as serving as a catalyst support for the production of heterogeneous catalytic converters. [7–10].

In recent years, precious metal immobilized on functionalized HCPs have attracted interested due to a range of significant advantages, including the ability to utilize a variety of synthesis methods, the presence of small pore size, excellent stability, low economic cost and optimum processing conditions [11, 12]. It was widely used in organic synthesis [13, 14], light/heterogeneous catalysis [15, 16], adsorption and separation [17, 18],  $CO_2$  conversion [19, 20] and other fields. Especially, as a heterogeneous catalyst in the field of organic synthesis, immobilization HCPs catalyst with precious metals has more advantages than traditional homogeneous catalysts, such as stable catalyst, mild reaction conditions, low emissions of three wastes, and low environmental pollution [21, 22]. Gu [23] synthesized the hyper-crosslinked organic polymers (HDS-3.6) by Friedel-Crafts alkylation, it exhibited the best results for ethyl levulinate formation with the optimal yield of 70.3%, and it did not significantly decrease in their catalytic properties. Lyubimov [24] developed a novel palladium nanoparticles catalyst by reduction of  $[Pd(\pi\text{-allyl})Cl]_2$  with hydrogen in a hyper-crosslinked polystyrene matrix. it showed high catalytic activity in the hydrogenation of benzene (benzene conversion was 100%). Nobre [25] obtained active catalysts by

combining Pd(OAc)<sub>2</sub> and iminophosphine ligands, which indicated high catalytic activity in Suzuki-Miyaura coupling reactions, high-yield coupling products can be obtained under mild conditions (25–50°C) using aryl bromide, iodide or benzyl chloride as substrates. Jia [26] prepared (HCP-PPh<sub>3</sub>-Ru) catalyst by a one-step external crosslinking reaction. It exhibited excellent catalytic activities in the synthesis of 2,4-diaryl substituted pyridine and diazodicarbonyl cycloaddition reaction. The results revealed that the ligand PPh<sub>3</sub> and Ru immobilised on HCP materials was quite robust in the organic transformations reaction.

Up to now, based on above mentioned investigated and our earlier experimental research on Suzuki-Miyaura coupling reactions [27–30], an efficient and stable palladium catalyst immobilized on functionalized hyper-crosslinked polymers had been successfully exploited. A convenient and environment-friendly method for the efficient synthesis of biphenyl and its derivatives from the organic coupling reaction had been successfully developed over HCPs-Pd catalyst. The research results from the catalytic Suzuki-Miyaura coupling reactions over palladium catalyst immobilized on functionalized hyper-crosslinked polymers are thoroughly reported in this paper.

## Experimental

### Reagents and instrument

8-hydroxyquinoline (AR, 99.0%), dimethoxy methane (AR, 98.0%), bromobenzene (AR, 99.5%), phenylboronic acid (AR, 98.0%) and iron chloride (AR, 99.9%) were obtained from Shanghai aladdin biochemical technology Co., Ltd, China. Benzene (AR, 99.7%) and 1,2-dichloroethane (AR, 99.5%) were purchased from Chengdu jinshan chemical Co., Ltd, China. Palladium chloride (AR, 98.0%) was obtained from Shanghai dibai biotechnology Co., Ltd, China. The other reagents were afforded commercially.

### Catalyst Preparation

( ) Synthesis of HCPs- [31]: AlCl<sub>3</sub> (anhydrous, 4.3601 g, 32.70 mmol ) and 8-hydroxyquinoline (0.5975 g, 4.12 mmol) were added to a solution of benzene (1.2165 g, 15.60 mmol) in 40 mL chloroform. The above formative mixture was stirred sufficiently at 20°C, then stirred at 45°C for 5.0 h in order to obtain the initial network, continued to raise the temperature to 80°C for 48 h to complete the reaction. The obtained precipitate after the reaction was washed 3 times with CH<sub>3</sub>OH, followed by hydrochloric acid in a Soxhlet for 24 h. pH of the product was modulated to neutralized with NaOH solution, then washed repeatedly with CH<sub>3</sub>OH in a Soxhlet for 55 h at 105°C, lastly vacuum dried at 60°C for 24 h (Defined as HCPs- ).

( ) Synthesis of HCPs- [32]: FeCl<sub>3</sub> (anhydrous, 3.3841 g, 20.86 mmol) was added to a solution of formaldehyde dimethyl acetal (FDA, 3.25 g, 42.72 mmol), benzene (1.2061 g, 15.46 mmol), 8-hydroxyquinoline (0.6083 g, 4.19 mmol) in 1,2-dichloroethane (DCE, 100 mL). The next experimental steps are similar to ( ) Synthesis of HCPs- . (Defined as HCPs- ).

( ) Preparation of HCPs-Pd [33]: The immobilized catalyst was obtained by the coordination of Palladium(II) ions with the HCPs ligand. Typically, HCPs (0.25 g) were added to the tetrahydrofuran solution (10 mL) containing Pd(OAc)<sub>2</sub> (0.037 g, 0.17 mmol), then refluxed at 60°C for 24 h. The next experimental steps are similar to ( ) Synthesis of HCPs- , and the catalyst as prepared was designated as HCPs- -Pd. For comparison, the HCPs- -Pd were prepared in the same way (As shown in Scheme 1).

## Catalyst characterizations

XPS spectroscopy was performed using an ESCALAB 250Xi spectrometer. The textural properties of the samples were afforded using the N<sub>2</sub> physisorption on an ASAP 2020 at 77K. The elemental content of the samples was analysed on a Thermo Scientific iCAP 7400 ICP-OES. FT-IR spectra of the samples were collected by using KBr matrix on a Nicolet-380 instrument (500–4000 cm<sup>-1</sup>). The HRTEM and SEM images were afforded on a JEM-2100 and Sigma HD, Carl Zeiss, Germany (FE-SEM), respectively.

## Typical Suzuki-Miyaura coupling reaction

The reactions were performed in a Schlenk reactor [34]. Typically, HCPs-Pd (20 mg) catalyst, bromobenzene (0.7801 g, 5.0 mmol), phenylboronic acid (0.7930 g, 6.5 mmol), and anhydrous K<sub>3</sub>PO<sub>4</sub> (1.6960 g, 8.0 mmol) were joined to solvent (15 mL, EtOH: H<sub>2</sub>O (4:1 v/v)) and reacted for 3.0 h at 80°C under N<sub>2</sub>. Bromobenzene was consumed as indicated by TLC, and poured into 100 mL ice water with stirring. The mixture was alternately washed with dichloromethane and water by turn (3×20 mL). The combined organic phase was filtered and concentrated under reduced pressure after MgSO<sub>4</sub> has adsorbed trace amounts of water. The obtained product was purified by flash chromatography (silica gel, light petroleum: diethyl ether = 20: 1) until biphenyl was obtained as a white solid (716.0 mg, 93.0%) (As shown in Scheme 2).

## Results and discussion

### Effects of reaction conditions on the reaction with bromobenzene and phenylboronic acid as raw material

The catalytic performances of HCPs-Pd catalyst with different solvent and base for the Suzuki-Miyaura reaction were examined (Table 1). Firstly, the influence of base species on the reaction process was investigated (**entries 1–3**), it shows that K<sub>3</sub>PO<sub>4</sub> has better effects than K<sub>2</sub>CO<sub>3</sub> and NaOH. Subsequently, different solvents were used for the reaction, it showed that 4/1 (v/v) CH<sub>3</sub>CH<sub>2</sub>OH and H<sub>2</sub>O solutions were the best with a yield of 93.0% (**entries 4–7**). Finally, other reaction conditions were explored (**entries 8–13**), including catalyst dosage, reaction temperature and time, no nitrogen protection and room temperature reaction. The optimal reaction conditions were obtained, 5.0 mmol bromobenzene, 6.5 mmol phenylboronic acid, 8.0 mmol base, 20 mg HCPs-Pd catalyst, 3.0 h, 80°C, the product yield reached 93.0%.

Table 1  
Exploration of reaction conditions <sup>a</sup>

Entry	Catalyst	Solvent	Base	Yield (%)
1	HCPs- -Pd	EtOH	K <sub>3</sub> PO <sub>4</sub>	84.3
2	HCPs- -Pd	EtOH	K <sub>2</sub> CO <sub>3</sub>	70.1
3	HCPs- -Pd	EtOH	NaOH	63.6
4	HCPs- -Pd	DMF	K <sub>3</sub> PO <sub>4</sub>	19.0
5	HCPs- -Pd	DMSO	K <sub>3</sub> PO <sub>4</sub>	23.5
6	HCPs- -Pd	H <sub>2</sub> O (TBAB,5%)	K <sub>3</sub> PO <sub>4</sub>	14.7
7	HCPs- -Pd	EtOH: H <sub>2</sub> O (4:1 v/v)	K <sub>3</sub> PO <sub>4</sub>	93.0
8 <sup>b</sup>	HCPs- -Pd	EtOH: H <sub>2</sub> O (4:1 v/v)	K <sub>3</sub> PO <sub>4</sub>	93.1
9 <sup>c</sup>	HCPs- -Pd	EtOH: H <sub>2</sub> O (1:1 v/v)	K <sub>3</sub> PO <sub>4</sub>	45.2
10	HCPs-I-Pd	EtOH: H <sub>2</sub> O (4:1 v/v)	K <sub>3</sub> PO <sub>4</sub>	82.4
11 <sup>d</sup>	HCPs- -Pd	EtOH: H <sub>2</sub> O (4:1 v/v)	K <sub>3</sub> PO <sub>4</sub>	65.2
12 <sup>e</sup>	HCPs- -Pd	EtOH: H <sub>2</sub> O (4:1 v/v)	K <sub>3</sub> PO <sub>4</sub>	77.5
13 <sup>f</sup>	HCPs- -Pd	EtOH: H <sub>2</sub> O (4:1 v/v)	K <sub>3</sub> PO <sub>4</sub>	28.7

<sup>a</sup> Reaction conditions: 5.0 mmol bromobenzene, 6.5 mmol phenylboronic acid, 8.0 mmol base, 20 mg HCPs-Pd catalyst, 3.0 h, 80°C, nitrogen protection.

<sup>b</sup> 40 mg HCPs-Pd catalyst.

<sup>c</sup> 10 mg HCPs-Pd catalyst.

<sup>d</sup> 1.0 h.

<sup>e</sup> Nitrogen protection: No.

<sup>f</sup> 12.0 h, room temperature.

## The recycle of HCPs-Pd catalyst and thermal filtration experiment in the reaction

The recycle of HCPs-Pd catalyst was studied under above optimum reaction conditions. The used catalyst was separated by centrifugation and washed several times in acetone and methanol. It was dried at 105°C and reused for the next reaction. Figure 1 shows the reusable results of the catalyst. It was evident that HCPs-Pd catalyst exhibited good stability in the reaction, 89.5% of biphenyl yield with high TON ( 2400) was still obtained after five runs.

In addition, in order to verify the absence of free palladium in the catalytic reaction system, two comparative experiments (normal reaction and reaction after thermal filtration of the catalyst) were conducted to further verify the stability of the catalyst [35]. For normal reactions, quenching was occurred after 1.0 h (Table 1, **entry 11**), and the final yield of biphenyl was 65.2%. Comparative experiment showed that after 1.0 h of reaction, the catalyst was removed by thermal filtration, and the reaction continued for 3.0 h. After quenching the reaction, the final yield of biphenyl was 66.7%. Furthermore, ICP testing was conducted on the filtered reaction solution, and the results showed that it did not contain Pd. Comparing two experiments, it was found that the change in product yield was relatively small, and the HCPs Pd catalyst did not shed palladium species, indicating good stability of the catalyst [36].

## Exploration of reactions with different substrates

Under the above conditions, a series of exploratory reactions were conducted to explore the catalytic reaction range of the catalyst (**Scheme 3**). As shown in Table 2, the catalytic reaction of HCPs-Pd has been proven to be suitable for the reactions of some compounds 1 and 2 containing different functional groups, resulting in the synthesis of product with high catalytic activity.

Table 2  
Catalytic performances for the Suzuki-Miyaura coupling reactions with different substrates

Entry	R <sup>1</sup>	X	R <sup>2</sup>	Target product	Yield (%)	TON
1	H	Br	H	3a	93.1	2543
2	H	Br	4-Me	3b	92.4	2524
3	H	Br	3-Me	3c	86.3	2358
4	H	Br	2-Me	3d	89.2	2437
5	H	Br	4-MeO	3e	90.7	2478
6	H	Br	2-F	3f	87.6	2393
7	H	Br	3-F	3g	83.5	2281
8	H	I	H	3a	95.2	2601
9	H	I	4-Me	3b	94.0	2568
10	4-Me	I	H	3b	88.5	2418
11	4-MeO	I	H	3e	91.9	2511
12	4-CN	I	H	3h	84.3	2303
13	2-CN-6-F	I	H	3i	81.8	2235
14	H	CH <sub>2</sub> Br	H	3j	82.4	2251
15	H	Cl	H	3a	0	0

## Catalyst characterization

N<sub>2</sub> adsorption desorption isotherms of four samples are shown in Fig. 2A. The typical type-IV isotherm with H4 hysteresis loop was observed for all samples [37]. In addition, the Non-Local Density Functional Theory method was used to get the pore diameter distribution curves (Fig. 2B). It can be evident that a regular distribution of the pore diameters in the micro- and meso-sizes is found for all samples [38].

Furthermore, the chemical composition and structural characteristics of the samples are listed in Table 3. The Pd content of the HCPs-Pd catalyst is essentially the same as that of the HCPs-Pd catalyst from the results of ICP test. The increased in pore volume and the decreased in BET specific surface area of HCPs-Pd may be due to the modification of Pd, which blocks the small pore size of HCPs [39]. These results indicated that hyper-crosslinked polymers containing palladium Pd components have been successfully prepared [39, 40].

Table 3  
Chemical composition and structural properties of samples

Samples	Pd(wt.%)	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (nm)
HCPs-	-	295.2	0.15	2.95
HCPs-	-	306.1	0.20	2.58
HCPs- -Pd	0.97	200.5	0.24	3.21
HCPs- -Pd	0.93	248.4	0.29	4.67

Figure 3 mainly explains XPS characterization of the Pd element in two HCPs-Pd samples. Figure 3A shows the characteristic peaks of C 1s and Pd 3d at binding energies 284.8 and 338.1 eV, respectively. It can be observed that both HCPs- -Pd and HCPs- -Pd exhibit the characteristic peaks of Pd. The complex Pd 3d spectra are shown in Fig. 3B. The presence of Pd(II) is correlated with the peaks at 343.7 and 338.2 eV, and the other peak at 342.2 and 336.6 eV are attributed to Pd(0), respectively [13, 15, 41]. It can be inferred that Pd has successfully coordinated with HCPs to form HCPs-Pd [41, 42].

SEM-Mapping was used to study the morphologies of four materials. As shown in Fig. 4, it indicated that HCPs- -Pd and HCPs- -Pd have no specific morphology, as if they are irregularly stacked spherical particles. To provide direct evidence of the successful introduction of Pd into HCPs, new evidence was obtained by elemental mapping of SEM images of two samples (Fig. 5) [43]. It indicates that the distribution of C, N, O and Pd can be clearly observed, confirming the existence and uniform distribution of Pd in two samples. It is worth noting that one of the reasons for its superior performance in the reaction process is the homogeneity of the four elements [44].

### 3.4.4 TEM

Figure 6 depicts the TEM images of four samples. The presence of Pd on hyper-crosslinked polymers is determined, and the lattice spacings of around 0.2 nm can be detected and attributed to the Pd species [45], as shown in the HRTEM images (Figs. 6B, 6D). The results demonstrate that the distribution of Pd species in HCPs-Pd samples is uniform. The uniform dispersion of active Pd species in the catalyst may be one reason for the good catalytic activity in the reaction [46–48].

FT-IR shows a large number of distinctive peaks of four samples (Fig. 7). Compared two curves of HCPs- and HCPs- -Pd, it is found that the intensity of the infrared peaks at 1624, 1492, 877 and 736 cm<sup>-1</sup> positions increased [49, 50]. Interestingly, compared the curves of HCPs- and HCPs- -Pd, it is found that the infrared peak of HCPs- -Pd shifted red at positions 782 and 736 cm<sup>-1</sup>, and is a separate infrared peak (741 cm<sup>-1</sup>). In addition, the peak intensity also weakens at 606 cm<sup>-1</sup> [51, 52]. These changes may be caused by the coordination of Pd on HCPs [53, 54].



# Conclusions

In conclusion, two porous hyper-crosslinked polymers (HCPs- , HCPs- ) were successfully designed and prepared by a one-pot Friedel-Crafts alkylation reaction employing anhydrous  $\text{FeCl}_3$  or  $\text{AlCl}_3$  in the presence or absence of FDA. Further, a “braided” strategy was used for the preparation of Pd metal-organic catalysts on functionalized HCPs. The new polymer (HCPs-Pd) has excellent catalytic activity, good porosity with high specific surface area, large pore volume, good stability and highly dispersed palladium. Consequently, in the Suzuki-Miyaura coupling reaction of aryl bromides, the HCPs-Pd showed good performance in combination with the mild conditions and hydrophilic reaction media. Furthermore, the HCPs-Pd catalyst can be recycled and reused for multiple runs with no apparent obvious loss of catalytic efficiency. This work also shows that the microporous polymers can not only act as supporting materials, but can also protect the catalyst and have a positive effect on the catalytic activity. In addition, we also expect the work to open up a new path of designing and constructing excellent heterogeneous solid catalysts on a molecular scale.

# Declarations

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## Author contribution

LF conceptualization, investigation, data curation, writing-original draft. SL writing & editing, data curation. HZ conceptualization, investigation, data curation. GC conceptualization, methodology, formal analysis, investigation, writing-original draft, writing-review & editing. DX conceptualization, supervision, project administration.

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## Data availability

All data generated or analyzed in this study are included in this article.

**Competing interests** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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

**Ethical approval** Not applicable.

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## Schemes

Schemes 1 to 3 are available in the Supplementary Files section.

## Figures

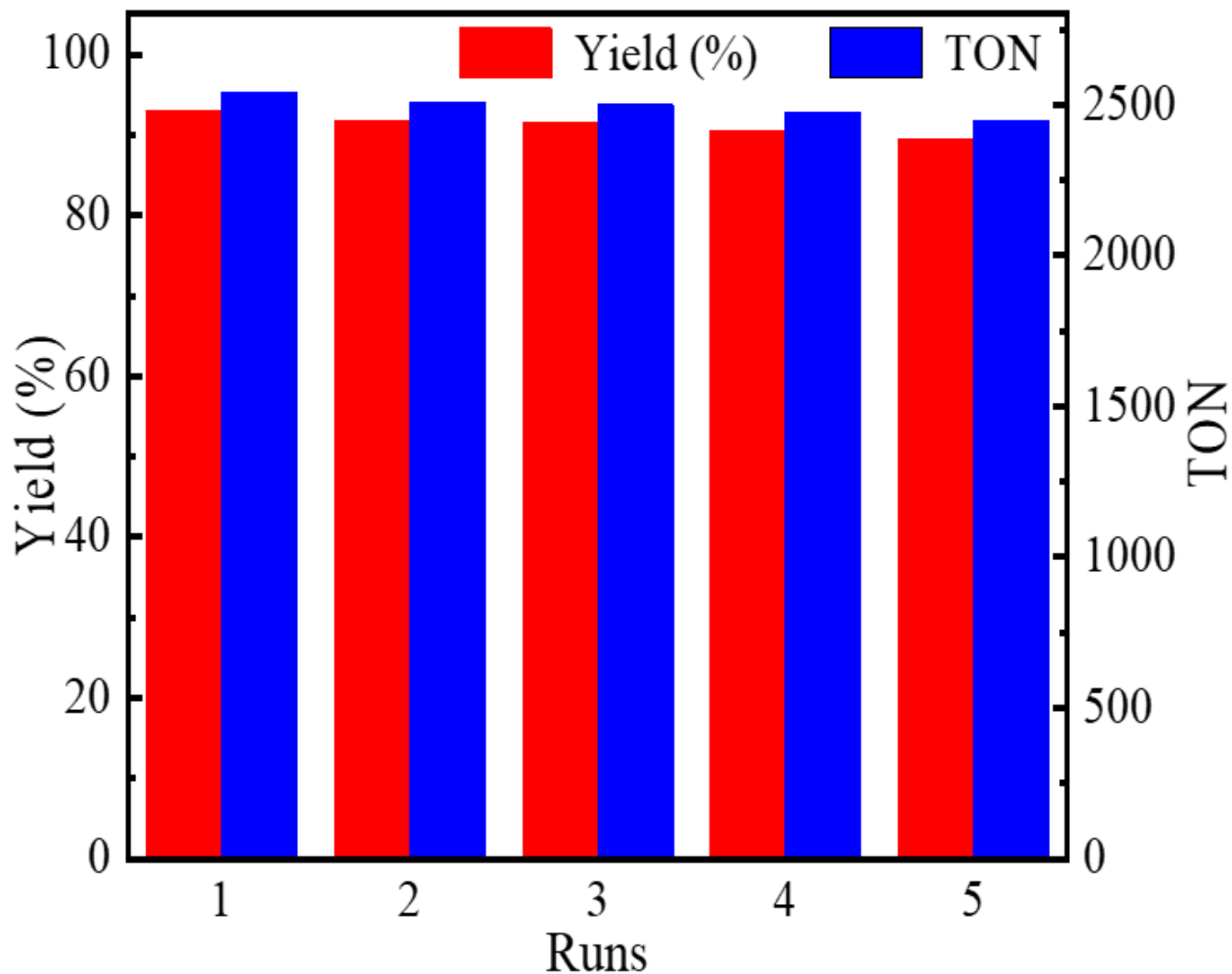
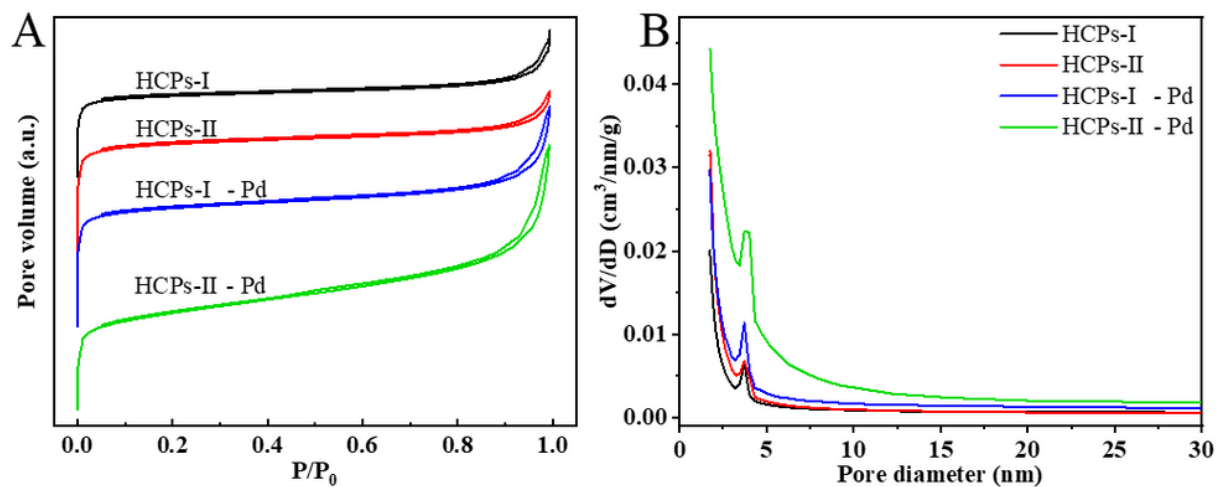


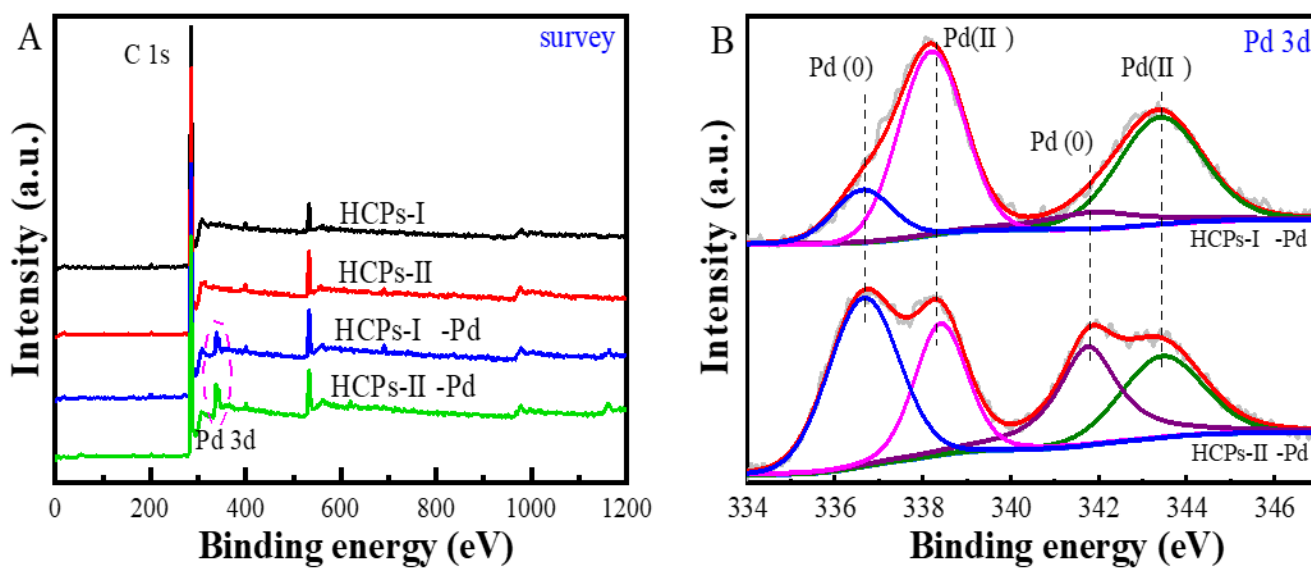
Figure 1

Results of recycle test of HCPs-Pd catalyst. Reaction conditions: bromobenzene (0.7800 g, 5.0 mmol), phenylboronic acid (0.7930 g, 6.5 mmol), anhydrous  $K_3PO_4$  (1.6960 g, 8.0 mmol) and EtOH:  $H_2O$  (4:1 v/v) solvent (15 mL), 3.0 h, 80 °C and HCPs-Pd (20 mg).



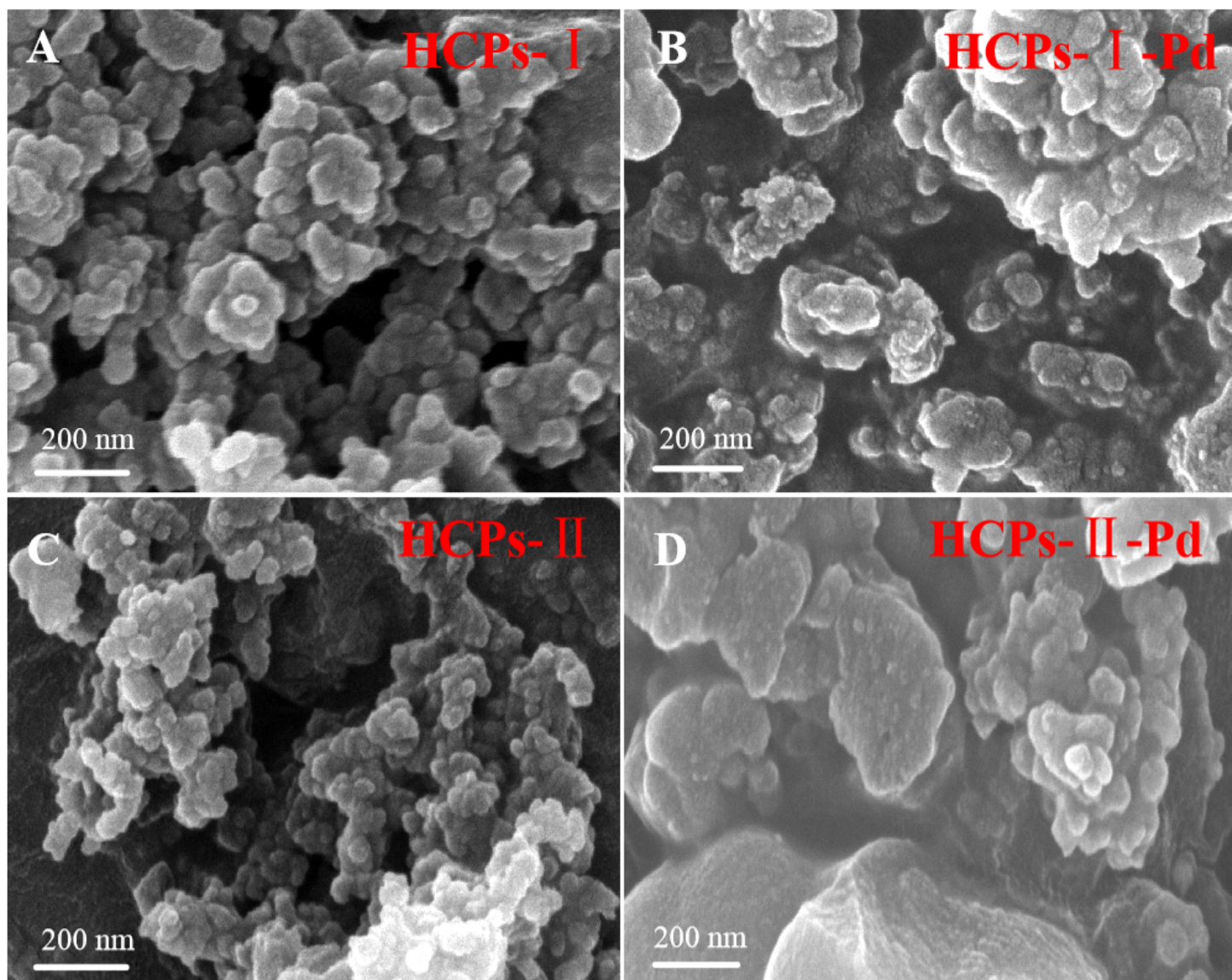
**Figure 2**

(A) N<sub>2</sub> adsorption-desorption isotherms and (B) pore diameter curves of samples.



**Figure 3**

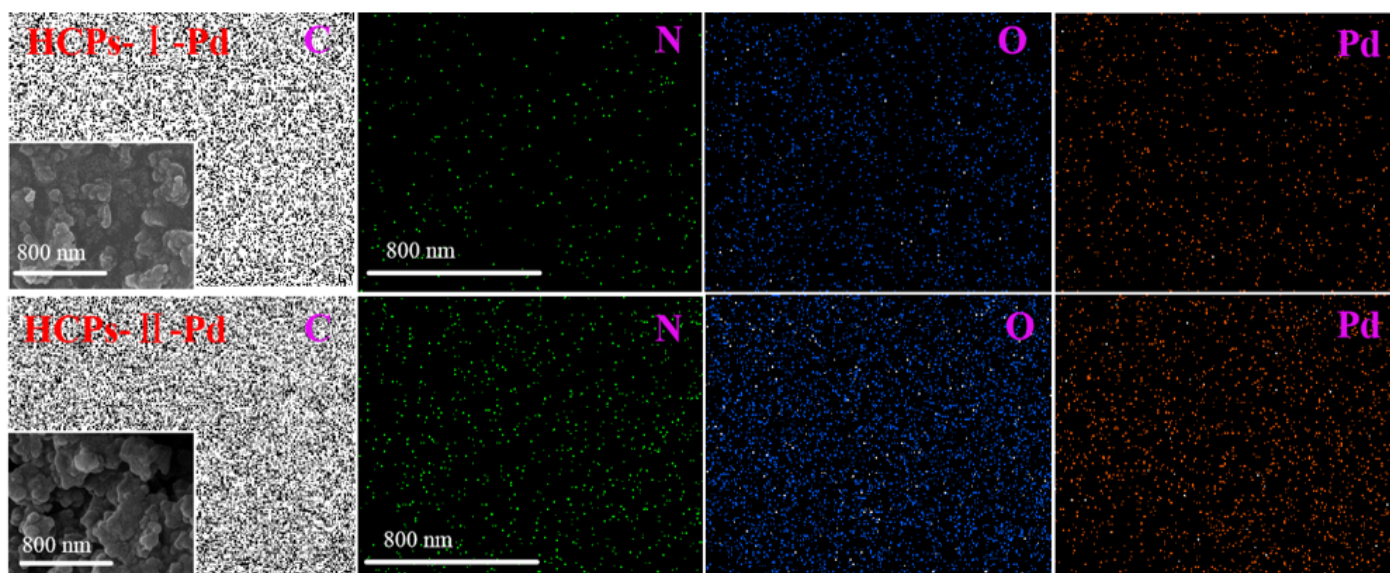
XPS spectra of samples.



**Figure 4**

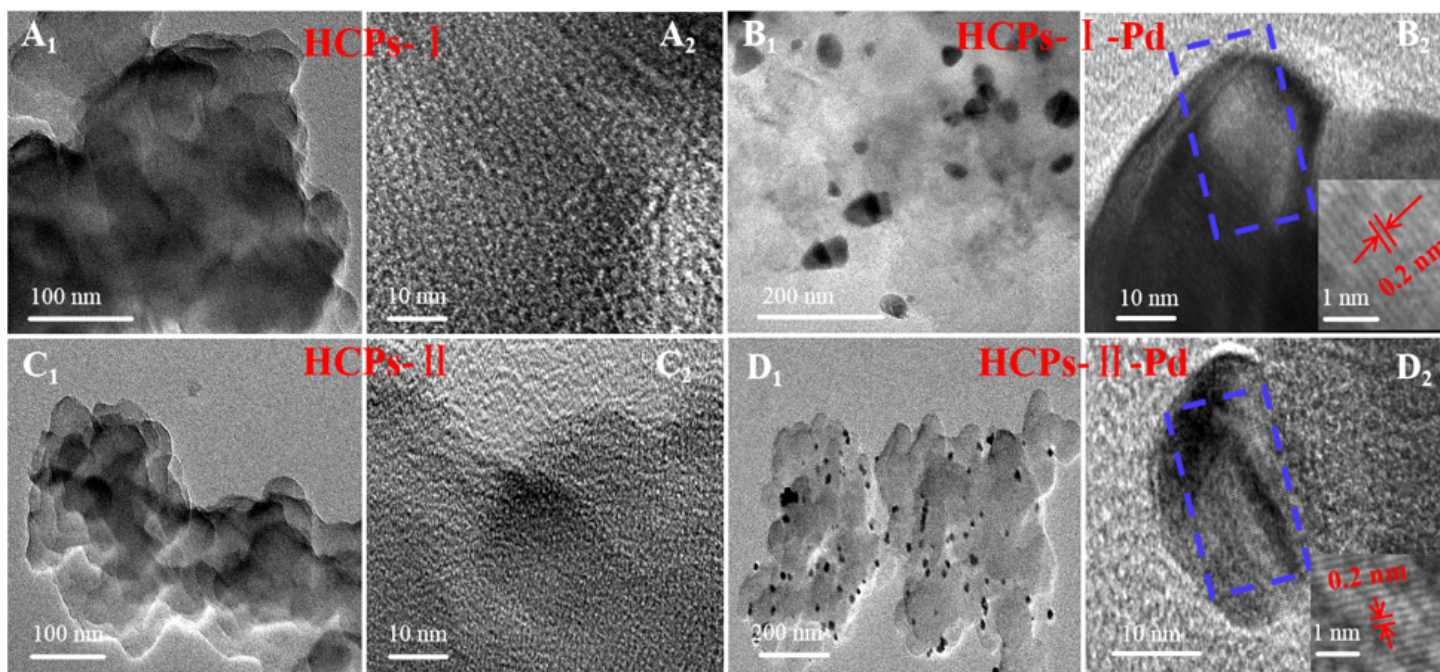
SEM images of samples.





**Figure 5**

SEM-Mapping images of HCPs-I-Pd and HCPs-II-Pd samples.



**Figure 6**

TEM images of samples.

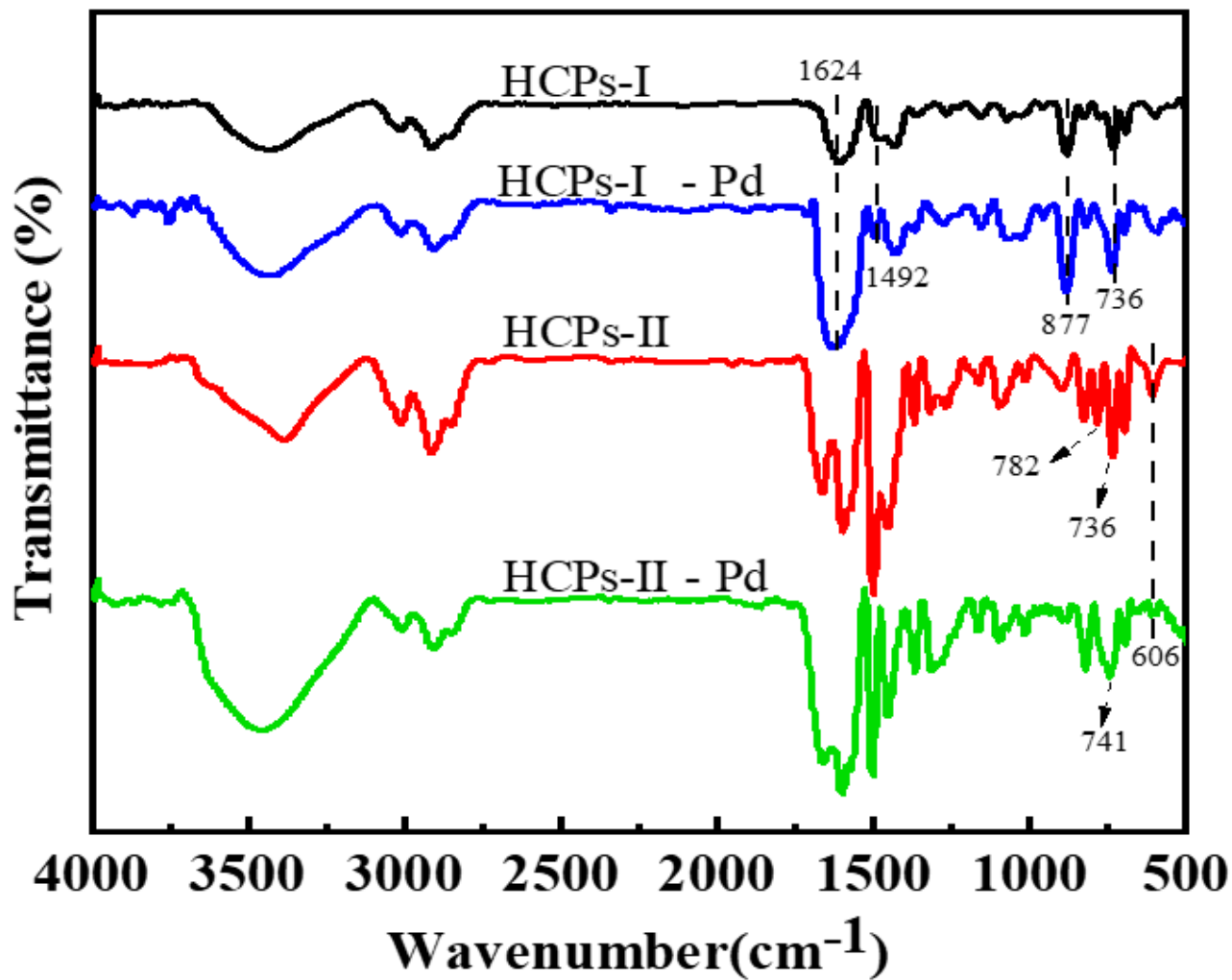


Figure 7

FT-IR curves of samples.

## Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [GA.png](#)
- [SC1.png](#)
- [SC2.png](#)
- [SC3.png](#)