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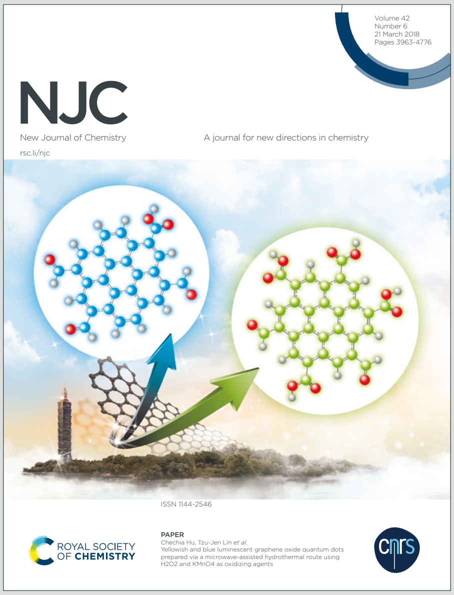

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PAPER
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Yellowish and blue luminescent graphene oxide quantum dots prepared via a microwave-assisted hydrothermal route using H2O2 and KMnO4 as oxidizing agents

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COMMUNICATION

Palladium immobilized on functionalized hypercrosslinked polymers: A highly active and recyclable catalyst for Suzuki-Miyaura coupling reactions in water

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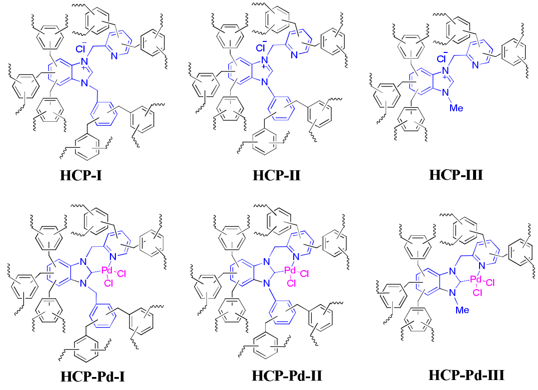
Xi Liu, Wei Xu, Dexuan Xiang,* Zaixing Zhang, Dizhao Chen, Yangjian Hu, Yuanxiang Li, Yuejun Ouyang, Hongwei Lin

Heterogeneous catalysts have shown advantages such as high stability, good recyclability and easy separation from reactants over homogeneous catalysts in recent years. In this paper, three pyridine-functionalized N-heterocyclic carbene-palladium complexes (HCP-Pd) were successfully synthesized through a simple external cross-linking reaction. In each catalyst (*i.e.*, complex), palladium (Pd) was immobilized on the hypercrosslinked polymer (HCP) via formation of a six-membered ring by Pd^{2+} and the bidentate ligands of NHC and pyridine. The structure and composition of HCP-Pd were characterized by SEM, TEM, N_2 sorption, FT-IR, TGA and XPS. The catalytic performances of these catalysts in Suzuki-Miyaura coupling reaction were also studied. The results prove that HCP-Pd is a very effective heterogeneous catalyst for the Suzuki-Miyaura coupling reaction of various aryl halides with aryl boronic acid in aqueous medium under mild conditions.

Heterogeneous catalysts have been extensively used for the catalysis of various organic reactions due to their unique properties such as high reactivity, high stability, easy separation, easy purification and good recyclability.[1] However, their catalytic efficiency and selectivity are normally lower than those of homogeneous systems because of their long diffusion pathway to catalytic sites and the difference of electron density on active sites.[2] This shortcoming can be overcome by using appropriate support materials that can provide a large reaction surface with more active sites.[3] Hypercrosslinked polymers (HCPs) with high specific surface area and large pore volume have already been regarded as superior supports for heterogeneous catalysts.[4] One distinct advantage of HCPs is that some electron-donating ligands can be installed in the skeletal framework without any additional chemical modification.[5]

N-heterocyclic carbenes (NHCs), also called "phosphine mimics" in catalysis, have attracted increasing attention as they have been proven to act as competent spectator ligands in coordination chemistry and catalysis.[6] There are numerous NHC-metal complexes acting as homogeneous catalysts for cross-coupling reactions with high yields of products.[7] In addition, a variety of supported NHC-metal complexes have been prepared[8] and include those supported on polymer,[9] nanoparticle,[10] carbon[11] and silica material.[12] Recently, a series of NHC-metal complexes supported on hypercrosslinked polymers (HCPs) by external cross-linking reaction were also reported.[5b,13] With high porosity and individual pore structures, the catalysts display outstanding catalytic performance in a wide range of organic synthetic reactions, such as Suzuki-Miyaura coupling, Ullmann C-N coupling, and Glaser coupling reactions. In these cases, NHC-metal complexes show higher thermal stability and catalytic activities than their phosphine counterparts partially owing to their strong σ-electron-donating ability that highly strengthens the NHC-metal bonds.[14]

Bidentate ligands containing both strong and weak donor groups are propitious to produce vacant coordination sites that allow complexation of substrates during the catalytic cycle, and at the same time the strong donor moiety remains connected to the metal center.[15] Pyridine-functionalised NHC (Py^NHC), as "classical" bidentate ligands, have been frequently used as homogeneous catalysts in recent years,[16] but only few supported Py^NHC-metal complexes have been prepared so far.[17] Therefore, it is desirable to exploit the diversity of immobilized Py^NHC-metal complexes and their application in downstream catalytic reactors.



Scheme 1 HCP and HCP-Pd

In this work, we designed and synthesised three pyridine-functionalized NHC-palladium complexes (HCP-Pd) by external crosslinking (Scheme 1). In each catalyst (*i.e.*, complex), palladium was immobilized on the hypercrosslinked polymer via formation of a six-membered ring by Pd^{2+} and the bidentate ligands of NHC and

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Hunan Engineering Laboratory for Preparation Technology of Polyvinyl Alcohol(PVA) Fiber Material, Institute of Organic Synthesis, Huaihua University, Huaihua 418000, China. E-mail: dexuanxiang@126.com

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pyridine. We then determined the catalytic properties of the catalysts in Suzuki-Miyaura coupling reactions under mild conditions in neat water as a solvent. The simple preparation of this porous catalyst and its high adaptability to various aryl halides and aryl boronic acid make it perfect catalytic option for Suzuki-Miyaura coupling reactions in water.

The supporting material HCP was prepared from *N*-(pyridin-2-ylmethyl)benzimidazolium chloride (NHC), FDA and benzene with $FeCl_3$ as catalyst. The following treatment of HCP with $PdCl_2$ in THF resulted in three kinds of HCP-Pd catalysts. The FT-IR spectra of HCP and HCP-Pd(Fig. 1) display a series of bands at around 1600-1700cm^{-1} which were assigned to the stretching of-C=N-in imidazolium ring. The bands at around 1550-1400 and 850-650cm^{-1} were corresponded to the benzene and pyridine skeleton stretching and the C-H out-of-plane bending vibrations of the aryl rings, respectively.

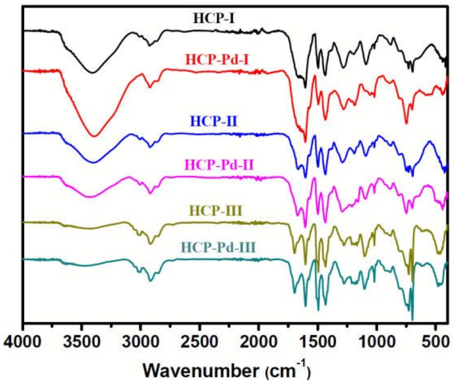

Figure 1. FT-IR spectra of HCP and HCP-Pd

XPS was employed to investigate the coordination states of palladium species, and the results are shown in ESI (Section V). The Pd 3d XPS spectra of the HCP-Pd-I catalyst reveal that Pd was present in the +2 oxidation state rather than in the metallic state, corresponding to the binding energy (B.E.) of 336.9 eV and 342.2 eV in the Pd 3d$_{5/2}$ and 3d$_{3/2}$ levels, respectively. Compared with the case of $PdCl_2$ (337.9 eV and 343.1eV), the Pd^{2+} binding energy in the HCP-Pd-I catalyst shifted negatively by 0.8 eV and 0.9 eV, which may be attributed to the strong coordination effect of the HCP network with bidentate ligands of NHC and pyridine groups. The results show that Pd^{2+} can be immobilized successfully on HCP by coordination to NHC and pyridine groups via forming a six-membered ring rather than by physical adsorption onto the surface of HCP. XPS graphs of HCP-Pd-II and III also reveal that Pd^{2+} was successfully immobilized on HCP materials.

The surface area and pore structure of HCP and HCP-Pd were investigated by nitrogen adsorption analysis at 77.3 K. As shown in Fig. 2, HCP-Pd exhibited type I adsorption-desorption isotherms, which were similar to the isotherms exhibited by the parent HCP, implying that these polymers contained both micropores and some mesopores. The apparent Brunauer-Emmett-Teller surface areas (S_{BET}) of HCP-Pd were smaller than those of the non-metallized parent networks (Table 1), but the materials were still significantly microporous. The decrease in specific surface area can be attributed to both partial pore filling and simple increase in mass. In addition, the pore size distribution of HCP remained almost unchanged after Pd was immobilized on it. The abundant micropores with a suitable size favored naturally the dispersion of the metal species. The presence of a few mesopores and macropores in the heterogeneous catalyst was also essential because these structures enabled the frameworks to be highly soaked in a certain solvent. As a result, the accessibility of the catalytically active sites toward the substrates can be maximized. The ICP-AES analysis indicates that the Pd loading in HCP-Pd I, II and III were 5.1, 6.6 and 5.5 wt% (Table 1), respectively.

Table 1 Physical properties of HCP and HCP-Pd

Sample	S_{BET}^{a} [m^2g^{-1}]	S_{Micro}^{b} [m^2g^{-1}]	V_{Micro}^{c} [m^3g^{-1}]	[Pd]^{d} [wt%]
HCP-I	693	352	0.159	-
HCP-Pd-I	648	366	0.170	5.1
HCP-II	774	656	0.274	-
HCP-Pd-II	610	483	0.215	6.6
HCP-III	667	358	0.159	-
HCP-Pd-III	600	256	0.132	5.5

[a] Surface area calculated from the nitrogen adsorption isothermusing the BET method. [b] Micropore volume derived using a t-plot methodbased on the Halsey thickness equation. [c] Total pore volume at P/P_0=0.99. [d] Data were obtained by inductively coupled plasma mass spectrometry (ICP-AES).

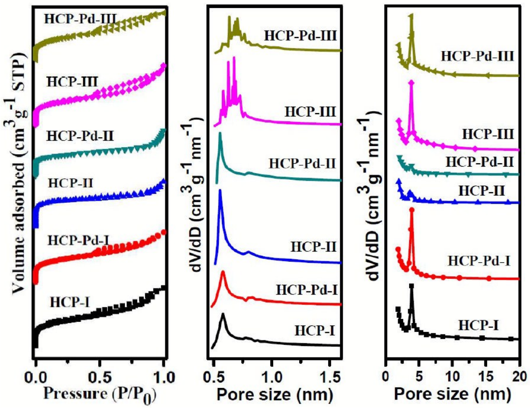

Figure 2.N_2 adsorption-desorption isotherms and corresponding pore size distributions of HCP and HCP-Pd.

The thermostability of HCP and HCP-Pd were also examined by thermogravimetric analysis (TGA). As shown in Fig. 3, these materials can remain stable at least up to a temperature less than 300°C. It seems that HCP-Pd was more stable than HCP when the temperature exceeded than 500°C, which may be ascribed to the six-membered ring formed by Pd^{2+} and the bidentate ligands of NHC and pyridine. It is worth mentioning that HCP-Pd-I showed the best thermostability and its loss of weight was less than 10% as the temperature reached 800°C.

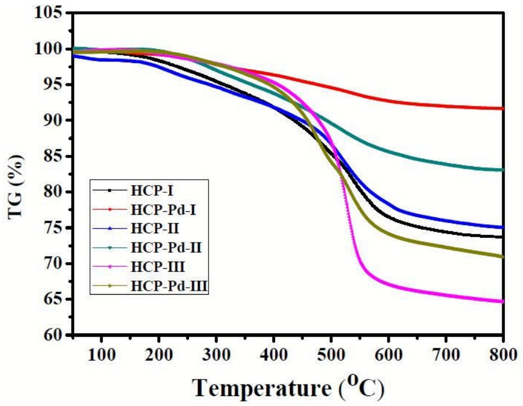

Figure 3. TGAcurves of HCP and HCP-Pd

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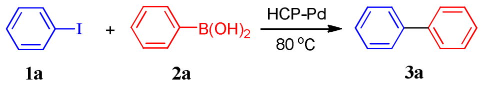
HCP and HCP-Pd were also subjected to SEM and TEM analyses (See ESI, Section III and IV). No remarkable changes in the morphologies of materials were observed after the palladium species were loaded. Then scanning electron microscopy elemental mapping was employed to study the composition of HCP-Pd, and the obtained results are shown in ESI (Section III and IV). Obviously, the metal Pd species were distributed in the support with a high degree of dispersion. Meanwhile, Pd, N and C were clearly observed from these images, which indicate that they were the major elements to construct the HCP-Pd catalyst.

To evaluate the activity of HCP-Pd catalysts, we utilized them in Suzuki-Miyaura coupling reaction under mild conditions. Our preliminary screening of solvent reveals that the presence of alcohol can efficiently promote the reaction (Table 2, Entry1-4). Some studies have shown that the addition of water to the solvent could speed up the conversion of substrate to some extent.[18] Then a range of reactions were carried out. Specifically, the feed volume ratio of EtOH to H_2O was changed from 3/1 to 1/3, and various bases like K_3PO_4, K_2CO_3 and Na_2CO_3 were tested. Some of the results are summarized in Table 2. Notably, there was nearly no obvious change in the yields of the reactions when H_2O content in solvent was increased. Since water is an easily available, cheap, safe and environmentally benign solvent, water was chosen here as solvent for the reaction and the reaction was found to proceed smoothly to achieve 95% yield of biaryl products (Entry10).

Table 2 Optimization of Suzuki-Miyaurareaction[a]



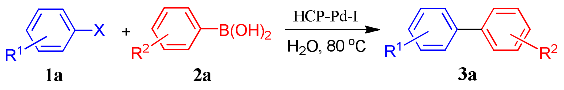
Entry	HCP-Pd	Solvent	Base	Yield(%)[b]
1	I	EtOH	K_3PO_4	96
2	I	CH_3CN	K_3PO_4	56
3	I	DMF	K_3PO_4	84
4	I	THF	K_3PO_4	47
5	I	EtOH/H_2O(3:1)	K_3PO_4	97
6	I	EtOH/H_2O(1:1)	K_3PO_4	98
7	I	EtOH/H_2O(1:3)	K_3PO_4	97
8	I	EtOH/H_2O(1:1)	K_2CO_3	88
9	I	EtOH/H_2O(1:1)	Na_2CO_3	85
10	I	H_2O	K_3PO_4	95
11	II	H_2O	K_3PO_4	90
12	III	H_2O	K_3PO_4	88
13	Poly-Pd	H_2O	K_3PO_4	86
14	$PdCl_2$/NHC[c]	H_2O	K_3PO_4	96

[a] Reaction conditions:1a (2.5 mmol), 2a (3.3mmol), HCP-Pd (40mg, 0.0115mmol), 80°C, 1.0h. [b] Isolated yields.[c] $PdCl_2$(0.5 mol%, 0.0125mmol), NHC-I(0.6 mol%, 0.015 mmol).

Furthermore, we also compared the ability of the three HCP-Pd catalysts to catalyze the Suzuki-Miyaura coupling reaction (Entry10-12). The results show that the highest yield of 95% can be obtained when the reaction of iodobenzene **1a** with phenyl boronic acid **2a** was conducted in the presence of K_3PO_4 in water with HCP-Pd-I as a catalyst. The reason that HCP-Pd-II and III was lower efficiency maybe attributed to their smaller pore size which caused the reactants to have to go through a long diffusion pathway to the catalytic sites.[2] To compare the catalytic properties between catalysts with monodentate and bidentate ligands, we synthesized the catalyst Poly-Pd with monomer *N,N'*-dibenzylbenzimidazolium chloride based on literature,[4b] and applied it in Suzuki-Miyaura reaction under the optimized condition to obtain a yield of 86% (Entry13). This result shows that HCP-Pd-I is more efficient than Poly-Pd in water, and the phenomenon maybe due to the fact that the pyridine group in HCP-Pd is more hydrophilic than the phenyl group in Poly-Pd.

With optimal conditions in hand, the reaction scope was examined. As listed in Table 3, a range of aryl boronic acids 2 with electron-donating group, such as 4-CH_3 (Table 5, entry 2), and electron-withdrawing group, such as 4-F (entry 6), were applied to these conditions in parallel. Corresponding biphenyl products were produced in high to excellent yields. It is worth noting that the cross-coupling reactions can proceed smoothly when aryl chloride and benzyl chloride were used in the reaction (entry 15-18).

Table 3 Suzuki-Miyaura reaction catalysed by HCP-Pd-I[a]



Entry	R^1	X	R^2	3	Yield(%)[b]
1	H	I	H	3a	95
2	H	I	2-CH_3	3b	96
3	H	I	3-CH_3	3c	92
4	H	I	4-CH_3	3d	97
5	H	I	2-F	3e	92
6	H	I	3-F	3f	93
7	H	I	4-F	3g	91
8	H	I	4-CN	3h	94
9	4-CH_3	I	H	3d	97
10	4-CH_3O	I	H	3i	98
11	H	Br	H	3a	95
12	H	Br	4-CH_3	3d	93
13	H	Br	4-F	3g	90
14	H	Br	4-CN	3h	91
15	H	Cl	H	3a	88
16	H	Cl	4-CH_3	3d	90
17	H	Cl	4-CN	3h	85
18	H	CH_2Cl	H	3j	87

[a] Reaction conditions:1a (2.5 mmol), 2a (3.3mmol), HCP-Pd-I (40mg), K_3PO_4(5.0 mmol), H_2O (20mL), 80°C, 1.0h. [b] Isolated yields.

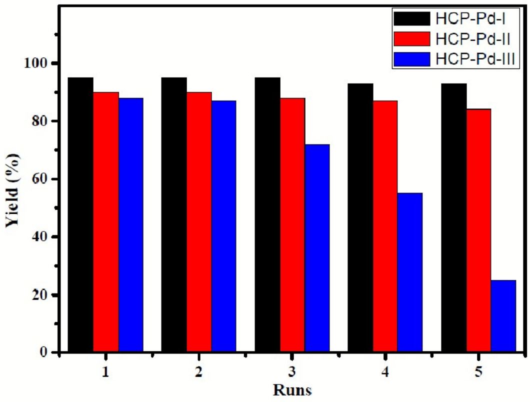


Figure 4. Recycle test of HCP-Pd in the Suzuki-Miyaura reaction

For supported catalysts, lifetime and recyclability are two important features. Therefore, we investigated the recycling performance of the HCP-Pd catalysts in Suzuki-Miyaura reaction, and the results are shown in Fig. 4. After five consecutive coupling reactions, HCP-Pd-I

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and II were still capable of catalyzing the reaction with yields of 93% and 84%, respectively, and the contents of Pd in HCP-Pd-I and II were 3.4% and 4.1%, respectively. In comparison, HCP-Pd-III was not as efficient as HCP-Pd-I and II, only affording the corresponding product in 25% yield, and the content of Pd containing in HCP-Pd-III decreased dramatically from 5.5% to 3.0%. This phenomenon may be attributed to the electronic effect of the substituent on the NHC and the cross-linked density of HCP. The stronger electron-withdrawing ability of the substituent resulted in more effective stabilization of the coordination bond of NHC-Pd^{2+}. Moreover, the catalysts HCP-Pd-I and II with benzyl and phenyl on NHC have more crosslinking sites which provide more efficient stabilization.

In sum, three pyridine-functionalized N-heterocyclic carbene-palladium complexes (HCP-Pd) were successfully synthesized through a simple external cross-linking reaction. In each catalyst (*i.e.*, complex), palladium was immobilized on the hypercrosslinked polymer via formation of a six-membered ring by Pd^{2+} and the bidentate ligands of NHC and pyridine. The microporous structure of the support ensures high dispersion of palladium active sites. The six-membered ring formed by Pd^{2+} and the bidentate ligands of NHC and pyridine makes Pd^{2+} presenthigh catalytic activity. As a result, the HCP-Pd catalyst exhibits outstanding catalytic performance in the Suzuki-Miyaura coupling reaction of various aryl halides with aryl boronic acid. In all the reactions, the HCP-Pd-I catalyst was found to be easily recovered and reused without significant loss of catalytic activity as compared with the HCP-Pd-II and III catalysts. Overall, this paper successfully prepared an effective and recyclable heterogeneous catalyst for the Suzuki-Miyaura coupling reaction of various aryl halides with aryl boronic acid in aqueous media under mild conditions.

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Conflicts of interest

The authors declare that there are no conflictsof interests.

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Palladium immobilized on functionalized hypercrosslinked polymers: A highly active and recyclable catalyst for Suzuki-Miyaura coupling reactions in water

Xi Liu, Wei Xu, Dexuan Xiang,* Zaixing Zhang, Dizhao Chen, Yangjian Hu, Yuanxiang Li, Yuejun Ouyang, Hongwei Lin

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Table of Contents

Three palladium complexes were synthesized through external cross-linking reaction and found to be effective heterogeneous catalysts for the Suzuki-Miyaura reaction.