Chinese Journal of Catalysis 37 (2016) 54–60

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Column on New Porous Catalytic Materials)

A Pd-metalated porous organic polymer as a highly efficient heterogeneous catalyst for C–C couplings

Zhifeng Dai, Fang Chen, Qi Sun, Yanyan Ji, Liang Wang, Xiangju Meng *, Feng-Shou Xiao

Key Laboratory of Applied Chemistry of Zhejiang Province and Department of Chemistry, Zhejiang University, Hangzhou 310028, Zhejiang, China

ARTICLE INFO

Article history:
Received 20 May 2015
Accepted 28 June 2015
Published 5 January 2016

Keywords:
Porous organic polymer
Phenanthroline ligand
Carbon–carbon couplings
Pd-based heterogeneous catalyst

ABSTRACT

An efficient catalyst system based on a Pd-metalated porous organic polymer bearing phenanthroline ligands was designed and synthesized. This catalyst was applied to various C–C bond-forming reactions, including the Suzuki, Heck and Sonogashira couplings, and afforded the corresponding products while exhibiting excellent activities and selectivities. More importantly, this catalyst can be readily recycled. These features show that such catalysts have significant potential applications in the future.

1. Introduction

Carbon–carbon bond forming reactions catalyzed by Pd species, such as the Suzuki, Heck and Sonogashira couplings, have been extremely important in the synthesis of pharmaceuticals and functionalized materials for some time now [1–8]. To promote these couplings, a wide range of homogeneous catalytic systems have been developed, some of which have achieved widespread acceptance due to their superior selectivity and activity, such that several have found industrial applications. Despite these achievements, the common usage of such coupling reactions in industrial processes has often been hindered by the complicated nature of the synthetic processes and the difficultly in recycling the catalyst [9,10]. To overcome these issues, a series of Pd-based heterogeneous catalysts have been developed, using a variety of insoluble supports, such as those based on carbon and silica [11,12]. However, carbon supports are relatively difficult to modify owing to their inert structures [13,14] and silica supports readily dissolve in alkaline media [15–17]. Therefore, it would be greatly beneficial to design highly stable, easily modified supports for the heterogenization of homogeneous catalysts.

Recently, porous organic polymers (POPs) exhibiting relatively good stability and capable of unique functionalization have emerged as an interesting class of materials with significant potential in the fields of gas storage, separation and catalysis [18–21]. In particular, POPs may act as highly tunable platforms, through the introduction of specific active species, for the development of extremely efficient heterogeneous catalysts with applications to various organic transformations [22–25].

More recently, we have shown that the stable, porous POP polydivinylbenzene (PDVB) can function as a powerful, insoluble support for the functionalization of catalytically active spe-

---

* Corresponding author. Tel/Fax: +86-571-88273698; E-mail: mengxj@zju.edu.cn

This work was supported by the National Natural Foundation of China (21422306, 21203165, 21403193) and the Fundamental Research Funds for the Central Universities (2015XZZX004-04).

DOI: 10.1016/S1872-2067(15)60952-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 1, January 2016

cies as heterogeneous catalysts [26]. In the present work, the rational synthesis of a POP containing phenanthroline ligands was attempted, through the copolymerization of divinylbenzene and vinyl-functionalized phenanthroline monomers under solvothermal conditions. The phenanthroline ligand was selected owing to its strong metal coordination ability and relatively high chemical stability [27–31]. After metalation with $Pd(OAc)_2$, the resulting heterogeneous catalyst exhibited excellent activity and recyclability during the Suzuki, Heck and Sonogashira coupling reactions.

2. Experimental

2.1. Sample synthesis

Solvents were purified according to standard laboratory methods; THF was distilled over sodium/benzophenone, DMF was distilled over calcium hydride, and $CHCl_3$ was distilled over anhydrous $CaCl_2$. Divinylbenzene (DVB), azobisisobutyronitrile (AIBN) and ethylbenzene were obtained from Tianjin Guangfu Chemical Reagents, whereas 1,10-phenanthroline monohydrate, $Pd(OAc)_2$, bromobenzene, phenylboronic acid, phenylacetylene and ethyl acrylate were purchased from the Aladdin Company, Ltd.

As shown in Scheme 1, a POP containing phenanthroline ligands (POP-Phen) was synthesized by the copolymerization of DVB with vinyl-functionalized phenanthroline monomers. In a typical reaction, 2.0 g DVB and 0.5 g vinyl-functionalized 1,10-phenanthroline (V-Phen) were dissolved in 20 mL DMF, followed by the addition of 0.05 g AIBN. The mixture was subsequently transferred to an autoclave and held for 24 h at 100 °C. After washing with ethanol, a solid orange product was obtained, denoted as POP-Phen herein [32].

The Pd-metalated POP (Pd/POP-Phen) catalyst was prepared by treating the POP-Phen with $Pd(OAc)_2$ in toluene. The mixture was initially stirred overnight at room temperature, followed by filtration of the solid product and washing with a significant quantity of toluene. After drying under vacuum at room temperature, the brown Pd-supported catalyst was obtained. Inductively coupled plasma optical emission spectroscopy (ICP-OES) determined that the Pd loading in the polymer was approximately 5.0% by weight.

2.2. Characterization

Nitrogen sorption isotherms at −196 °C were acquired using Micromeritics ASAP 2020M and Tristar systems. The samples were outgassed for 10 h at 100 °C prior to these measurements. Scanning electron microscopy (SEM) was performed using a Hitachi SU1510 and SU4800 and transmission electron microscopy (TEM) was carried out with a Hitachi HT-7700. X-ray photoelectron spectroscopy (XPS) spectra were acquired on a Thermo ESCALAB 250 with Al K irradiation at $\theta = 90°$ and the binding energies were calibrated using the C1*s* peak at 284.9 eV. ICP-OES analysis was performed with a PerkinElmer plasma 40 emission spectrometer and ^{1}H NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer, with chemical shifts expressed in ppm downfield from TMS at $\delta = 0$ ppm. ^{13}C (100.5 MHz) magic angle spinning (MAS) NMR spectra were recorded on a Varian infinity plus 400 spectrometer equipped with a magic angle spin probe and a 4-mm ZrO_2 rotor.

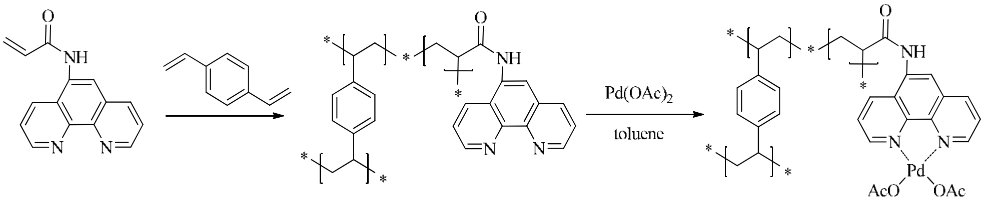
2.3. Catalytic tests

In a typical Suzuki coupling, 1 mmol halide, 1.2 mmol phenylboronic acid, 1.5 mmol $K_3PO_4·3H_2O$, 0.01 g catalyst, 3 mL water and 2 mL ethanol were reacted at 80–120 °C with constant stirring. A typical Heck coupling used 1 mmol halide, 1.2 mmol vinylic substrate, 1.5 mmol $K_3PO_4·3H_2O$, 0.01 g catalyst and 5 mL NMP (1-methy-2-pyrrolidinone) at 130–140 °C. In a typical Sonogashira coupling, 1 mmol halide, 1.2 mmol benzyne, 1.5 mmol $K_3PO_4·3H_2O$, 0.01 g catalyst and 5 mL solvent were used at 120–140 °C. After each reaction, the catalyst was removed by centrifugation and analyzed by gas chromatography (GC-1690, Kexiao Co.) using a flame ionization detector and a DB-1 capillary column.

3. Results and discussion

3.1. Characterization

Figure 1 shows the ^{13}C MAS NMR and IR spectra of the PDVB and POP-Phen samples. In the ^{13}C MAS NMR spectra of the POP-Phen, two peaks are seen at 163 and 175 ppm, both of which are associated with C=O and C=N bonds in the V-Phen component [33–36]. The IR spectrum of POP-Phen displays a strong band at 1698 cm^{-1} that is assigned to the V-Phen C=O bond [32]. These results indicate successful incorporation of the 1,10-phenanthroline ligand into the sample. Furthermore, TG analysis found that the mass loss of the POP-Phen occured above 360 °C, associated with decomposition of the polymer skeleton, indicating its superior thermal stability. N_2 sorption isotherms revealed that both POP-Phen and Pd/POP-Phen (Fig. 2(a)) generated a hysteresis loop over the relative pressure range of 0.45 to 0.95, demonstrating the presence of mesopores in the samples. The sample pore sizes were primarily distrib-



Scheme 1. Structure and synthetic procedures for the preparation of Pd/PCP-Phen.

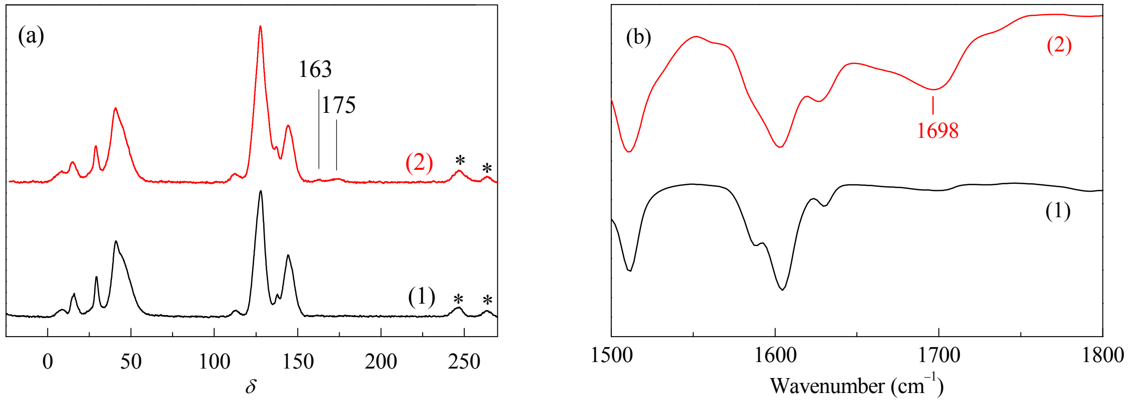


Fig. 1. ^{13}C MAS NMR (a) and IR spectra (b) of PDVB (1) and POP-Phen samples (2).

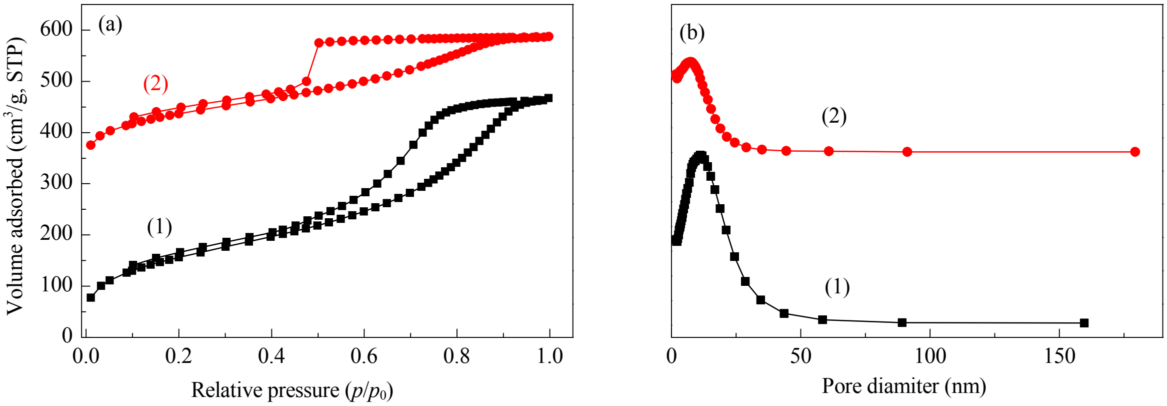


Fig. 2. N_2 sorption isotherms (a) and pore size distributions (b) of POP-Phen (1) and Pd/POP-Phen (2) samples. The Pd/POP-Phen isotherm and pore size distribution have been offset by 300 cm^3/g and 0.70 cm^3/g along the vertical axis, respectively, for clarity.

uted around means of 11.2 and 7.3 nm in the POP-Phen and Pd/POP-Phen, respectively (Fig. 2(b)), as calculated by the Barrett–Joyner–Halenda (BJH) method. The BET surface areas of the specimens were estimated to be 574 and 462 m^2/g. SEM (Figs. 3(a, b)) and TEM images (Figs. 3(c, d)) of the POP-Phen and Pd/POP-Phen give direct evidence of the abundant mesoporosity, in good agreement with the N_2 sorption results. Obviously, the presence of mesoporous structures in the samples is beneficial with regard to mass transfer during reaction.

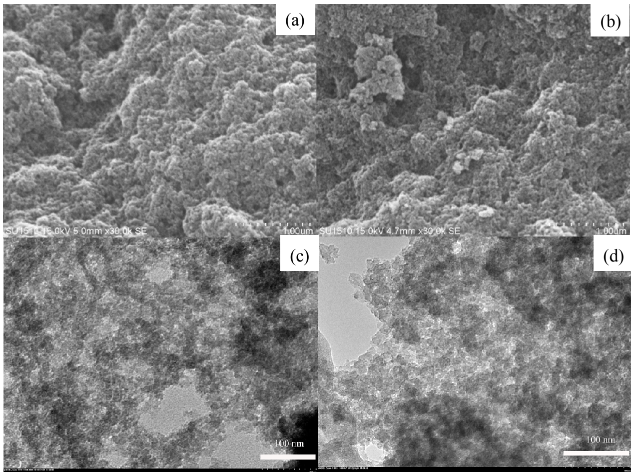


Fig. 3. SEM (a, b) and TEM (c, d) images of POP-Phen (a, c) and Pd/POP-Phen (b, d) samples.

Figure 4 presents XPS data, in which the Pd/POP-Phen sample is seen to generate Pd 3$d_{5/2}$ and Pd 3$d_{3/2}$ peaks at 337.6 and 343.1 e V, values that are lower than those of Pd(OAc)$_2$ (338.6 and 343.8 eV, Fig. 4(a)). At the same time, the Pd/POP-Phen sample exhibits an N 1*s* peak at 400.0 eV that is obviously located higher than that of the POP-Phen (399.3 eV, Fig. 4(b)). These results strongly support coordination between 1,10-phenanthroline moieties in the POP-Phen and Pd species [29].

3.2. Evaluation of catalytic performance

Table 1 presents the Suzuki, Sonogashira and Heck coupling reaction results over the Pd/POP-Phen catalyst. During the Suzuki coupling, when bromobenzene and phenylboronic acid were used as the reactants and a mixture of ethanol and water was employed as the solvent, a very high yield of biphenyl (> 99%) was obtained in a short reaction time (30 min, entry 1). In contrast, the corresponding Pd-based homogeneous catalyst showed a very low yield (1.7%) under the same conditions (entry 2). These results indicate that the Pd/POP-Phen catalyst is very active for Suzuki coupling. More importantly, the Pd/POP-Phen catalyst exhibited excellent recyclability. After

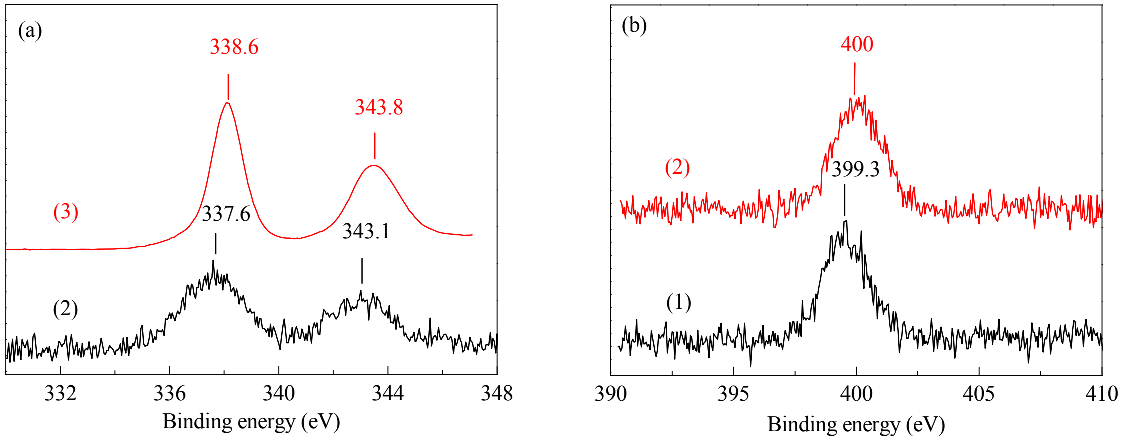
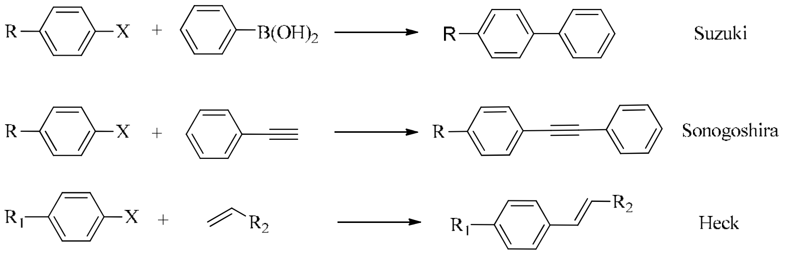
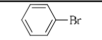
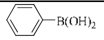
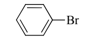
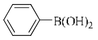
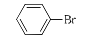
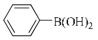
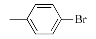
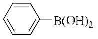
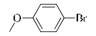
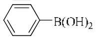
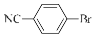
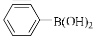
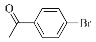
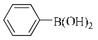
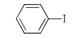
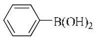
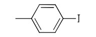
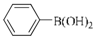
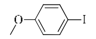
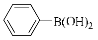
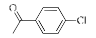
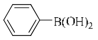
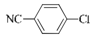
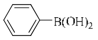
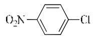
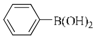
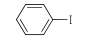
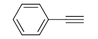
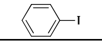
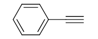
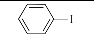
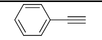
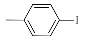
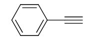
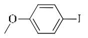
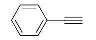
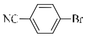
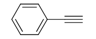
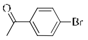
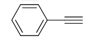
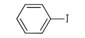
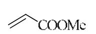
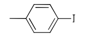
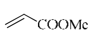
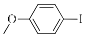
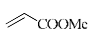
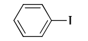
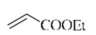
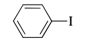
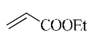
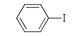
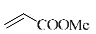
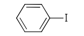
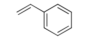
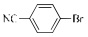
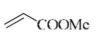
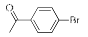
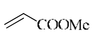


Fig. 4. Pd 3*d* (a) and N 1*s* (b) spectra of POP-Phen (1), Pd/POP-Phen (2) and Pd(OAc)$_2$ (3).

five recycling trials, no significant loss of the catalytic activity was observed (entry 3). In addition, no residual Pd species were detected in the filtered reaction mixture (results below the limit of detection of the ICP-OES analysis, <10 ppb), suggesting that there was no leaching of Pd from the catalyst. This result may be reasonably attributed to the strong coordination between the Pd species and the phenanthroline moieties, as observed in Fig. 4.

Table 1
Results of Suzuki, Sonogashira and Heck couplings over the Pd/POP-Phen catalyst[a].



Reaction	Entry	Aryl halide	Coupling substrate	Yield[b] (%)
Suzuki	1			99
	2[c]			1.7
	3[d]			97
	4			95
	5			96
	6			99
	7			99
	8[e]			98
	9[e]			94
	10[e]			99
	11[f]			24
	12[f]			32
	13[f]			34
Sonogashira	14			99
	15[c]			93
	16[d]			95
	17			99
	18			99
	19[g]			98
	20[g]			96
Heck	21			99
	22			99
	23			99
	24			99
	25[c]			43
	26[d]			99
	27[g]			99
	28[g]			99
	29[g]			97

[a] Suzuki conditions: halide1 mmol, phenylboronic acid 1.2 mmol, K$_3$PO$_4$·3H$_2$O 2 mmol, catalyst 0.01 g, water 3 mL, ethanol 2 mL, 80 °C, 30 min; Sonogashira conditions: halide 1 mmol, benzyne 1.2 mmol, K$_3$PO$_4$·3H$_2$O 1.5 mmol, catalyst 0.01 g, butanol 5 mL, 120 °C, 30 min; Heck conditions: halide 1 mmol, vinylic substrate 1.2 mmol, K$_3$PO$_4$·3H$_2$O 1.5 mmol, catalyst 0.01 g, NMP (1-methy-2-pyrrolidinone) 5 mL, 130 °C, 20 min.

[b] GC yield.

[c] 1 mg Pd(OAc)$_2$ and 0.9 mg 1,10-phenanthroline as a homogeneous catalyst.

[d] Recycled five times.

[e] Reaction time 20 min.

[f] Reaction conditions: halide 1 mmol, phenylboronic acid 1.2 mmol, KOH 2 mmol, catalyst 0.05 g, water 5 mL, 120 °C, 2 h.

[g] 140 °C, 30 min.

A series of substrates was applied to the Suzuki coupling reaction over the Pd/POP-Phen catalyst (Table 1, entries 4-13). Notably, the use of aryl bromides generated excellent yields from both electron-poor and electron-rich reagents (94%–99%, entries 4–10). However, in the case of the less reactive aryl chlorides, the catalytic activity of the Pd/POP-Phen was insufficient, affording relatively low yields (24%–34%) even when the reactions were carried out at a higher temperature (120 °C), over a longer reaction time (2 h) and with a higher catalyst loading (0.05 g, entries 11–13). Therefore, some limitations still remain regarding the Suzuki reaction catalyzed by the Pd/POP-Phen catalyst.

In Sonogashira coupling, the Pd/POP-Phen catalyst was also found to be very active. Using iodobenzene as the substrate, a yield of 99% was obtained (entry 14). This value is somewhat higher than the yield of 93% obtained from the corresponding homogeneous catalyst (entry 15). In addition, iodotoluene and iodoanisole both gave yields of 99% (entries 17 and 18) and, when aryl bromides were employed as substrates, the yields were as high as 96%–99% even in the absence of the CuI co-catalyst (entries 19 and 20). The absence of the CuI completely avoids the formation of the diyne by-product that is usually formed from an acetylene homocoupling side reaction [37–39]. After five recycling trials, a yield of 95% could still be obtained from the catalyst (entry 16).

In the case of Heck coupling, the Pd/POP-Phen catalyst once again exhibited very high activity and selectivity. As an example, aryl iodides could be fully converted over short time intervals of 20 to 30 min, giving yields up to 99% (entries 21–24 and 27). These values are obviously higher than that obtained from the corresponding homogeneous catalyst (entry 25). When aryl bromides were employed, the yields were still in the range of 97%–99% after 30 min (entries 28 and 29). The catalyst was also found, once again, to be recyclable and produced a yield of 99% following five recycling trials (entry 26).

It is worth noting that the Pd/POP-Phen heterogeneous catalyst exhibited higher activities than the homogeneous Pd/Phen catalyst in these reactions, which may be attributed to the differences in the reactant concentrations between the catalysts. In the case of the heterogeneous catalyst, the catalytic material is highly porous, resulting in a much higher reactant concentration in the catalyst pores compared with that on the homogeneous catalyst. During the Suzuki coupling, for example, the bromobenzene concentration in the pores of the Pd/POP-Phen catalyst was almost 14 times the concentration in the Pd/Phen system. According to the Arrhenius equation, higher reactant concentrations should give rise to higher catalytic activity, which is consistent with previously reported results [40].

4. Conclusions

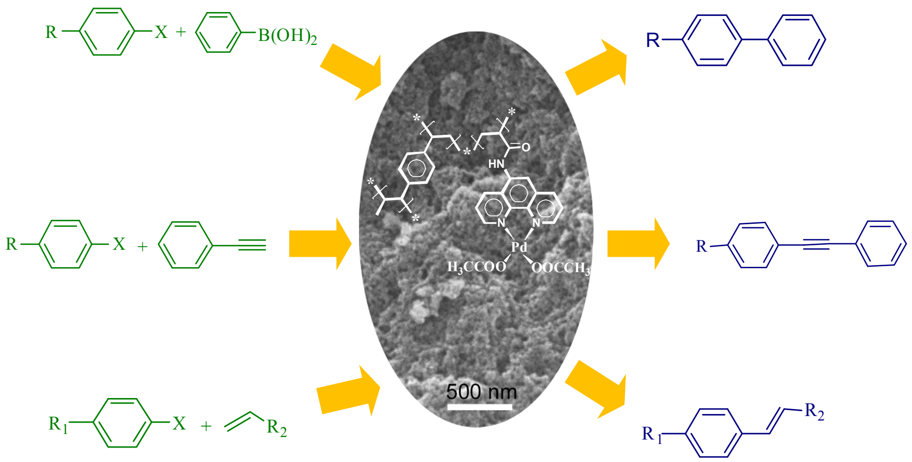
In summary, a novel strategy for the preparation of highly efficient Pd-based heterogeneous catalysts using porous organic polymers containing phenanthroline moieties has been demonstrated. This catalyst not only exhibits excellent catalytic activity but also outstanding stability as well as superior recyclability in Suzuki, Sonogashira and Heck couplings. These characteristics are important with regard to developing practical syntheses of fine chemicals in the future.

Graphical Abstract

Chin. J. Catal., 2016, 37: 54–60 doi: 10.1016/S1872-2067(15)60952-4

A Pd-metalated porous organic polymer as a highly efficient heterogeneous catalyst for C–C couplings

Zhifeng Dai, Fang Chen, Qi Sun, Yanyan Ji, Liang Wang, Xiangju Meng*, Feng-Shou Xiao
Zhejiang University



A Pd-metalated porous polymer bearing phenanthroline moieties (Pd/POP-Phen) exhibits high activities, excellent selectivities and superior recyclabilities in Suzuki, Sonogashira and Heck couplings.

References

[1] F. Diederich, A. de Meijere, *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed., Wiley-VCH, Weinheim, **2004**, 4.
[2] L. X. Yin, J. Liebscher, *Chem. Rev.*, **2007**, 107, 133.
[3] N. Miyaura, A. Suzuki, *Chem. Rev.,* **1995**, 95, 2457.
[4] C. M. Wei, C. J. Li, *J. Am. Chem. Soc.,* **2003**, 125, 9584.
[5] J. Magano, J. R. Dunetz, *Chem. Rev.*, **2011**, 111, 2177.
[6] N. E. Leadbeater, M. Marco, *Chem. Rev.*, **2002**, 102, 3217.
[7] W. Watanabe, T. Maekawa, Y. Miyazaki, T. Kida, K. Takeshita, A. Mori, *Chem Asian J.*, **2012**, 7, 1679.
[8] M. Bakherad, A. Keivanloo, S. Samangooei, *Chin. J. Catal.*, **2014**, 35, 324.
[9] C. E. Garrett, K. Prasad, *Adv. Synth. Catal.*, **2004**, 346, 889.
[10] C. J. Welch, J. Albaneze-Walker, W. R. Leonard, M. Biba, J. DaSilva, D. Henderson, B. Laing, D. J. Mathre, S. Spencer, X. D. Bu, T. B. Wang, *Org. Process Res. Dev.*, **2005**, 9, 198.
[11] H. U. Blaser, A. Indolese, A. Schnyder, H. Steiner, M. Studer, *J. Mol. Catal. A*, **2001**, 173, 3.
[12] B. M. Bhanage, M. Arai, *Catal. Rev.*, **2001**, 43, 315.
[13] X. Jin, V. V. Balasubramanian, S. T. Selvan, D. P. Sawant, M. A. Chari, G. Q. Lu, A. Vinu, *Angew. Chem. Int. Ed.*, **2009**, 48, 7884.
[14] M. Kawaguchi, S. Yagi, H. Enomoto, *Carbon*, **2004**, 42, 345.
[15] Q. H. Fan, Y. M. Li, A. S. C. Chan, *Chem. Rev.*, **2002**, 102, 3385.
[16] S. Minakata, M. Komatsu, *Chem. Rev.*, **2009**, 109, 711.
[17] D. E. De Vos, M. Dams, B. F. Sels, P. A. Jacobs, *Chem. Rev.*, **2002**, 102, 3615.
[18] A. Taguchi, F. Schuth, *Microporous Mesoporous Mater.*, **2005**, 77, 1.
[19] M. Hartmann, *Chem. Mater.*, **2005**, 17, 4577.
[20] A. Corma, H. Garcia, *Adv. Synth. Catal.*, **2006**, 348, 1391.
[21] A. Thomas, *Angew. Chem. Int. Ed.*, **2010**, 49, 8328.
[22] Q. Sun, M. Jiang, Z. J. Shen, Y. Y. Jin, S. X. Pan, L. Wang, X. J. Meng, W. Z. Chen, Y. J. Ding, J. X. Li, F-S. Xiao, *Chem. Commun.*, **2014**, 50, 11844.
[23] Q. Sun, Z. F. Dai, X. L. Liu, N. Sheng, F. Deng, X. J. Meng, F-S. Xiao, *J. Am. Chem. Soc.*, **2015**, 137, 5204.
[24] Q. Sun, X. J. Meng, X. L. Liu, X. M. Zhang, Y. Yang, Q. H. Yang, F-S. Xiao, *Chem. Commun.,* **2012**, 48, 10505.
[25] Y. Huangfu, Q. Sun, S. X. Pan, X. J. Meng, F-S. Xiao, *ACS Catal.*, **2015**, 5, 1556.
[26] C. Bleschke, J. Schmidt, D. S. Kundu, S. Blechert, A. Thomas, *Adv. Synth. Catal.*, **2011**, 353, 3101.
[27] J. D. Crowley, S. M. Goldup, N. D. Gowans, D. A. Leigh, V. E. Ronaldson, A. M. Z. Slawin, *J. Am. Chem. Soc.*, **2010**, 132, 6243.
[28] T. Hamada, X. Ye, S. S. Stahl, *J. Am. Chem. Soc.*, **2008**, 130, 833.
[29] M. Boltz, A. Blanc, G. Laugel, P. Pale, B. Louis, *Chin. J. Catal.*, **2011**, 32, 807.
[30] J. L. Hu, Y. L. Gu, Z. H. Guan, J. J. Li, W. L. Mo, T. Li, G. X. Li, *ChemSusChem*, **2011**, 4, 1767.
[31] Y. X. Gao, G. Wang, L. Chen, P. X. Xu, Y. F. Zhao, Y. B. Zhou, L. B. Han, *J. Am. Chem. Soc.*, **2009**, 131, 7956.
[32] Q. Sun, Z. F. Lv, Y. Y. Du, Q. M. Wu, L. Wang, L. F. Zhu, X. J. Meng, W. Z. Chen, F-S. Xiao, *Chem. Asian J.*, **2013**, 8, 2822.
[33] J. P. Lecomte, A. Kirsch-De Mesmaeker, M. Demeunynck, J. Lhomme, *J. Chem. Soc.*, *Faraday Trans.*, **1993**, 89, 3261.
[34] W. H. Lin, W. L. Sun, J. Yang, Q. H. Sun, Z. Q. Shen, *J. Phys. Chem. C*, **2009**, 113, 16884.
[35] M. B. Majewski, N. R. de Tacconi, F. M. MacDonnell, M. O. Wolf, *Inorg. Chem.*, **2011**, 50, 9939.
[36] X. Y. Liu, Y. L. Hu, B. Y. Wang, Z. X. Su, *Synth. Metals*, **2009**, 159, 1557.
[37] P. Siemsen, R. C. Livingston, F. Diederich, *Angew. Chem. Int. Ed.*, **2000**, 39, 2632
[38] A. Elangovan, Y. H. Wang, T. I. Ho, *Org. Lett.*, **2003**, 5, 1841.
[39] S. Thorand, N. Krause, *J. Org. Chem.*, **1998**, 63, 8551.
[40] F. J. Liu, L. Wang, Q. Sun, L. F. Zhu, X. J. Meng, F. S. Xiao, *J. Am. Chem. Soc.*, **2012**, 134, 16948.

Page numbers refer to the contents in the print version, which include both the English version and extended Chinese abstract of the paper. The online version only has the English version. The pages with the extended Chinese abstract are only available in the print version.