

Available online at www.sciencedirect.com



CHINESE Chemical Letters

Chinese Chemical Letters 21 (2010) 1062-1066

www.elsevier.com/locate/cclet

Macroporous magnetic poly(GMA-EGDMA-DVB) microspheres supported palladium complex as an efficient catalyst for Heck reaction

Ding Zhong Yuan, Qiu Yu Zhang*, Jin Bo Dou

Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an 710129, China Received 30 December 2009

Abstract

Macroporous magnetic poly(GMA-EGDMA-DVB) microspheres synthesized by suspension polymerization were used as supports for palladium catalyst. The results showed the novel magnetic catalyst can promote Heck reaction of aryl halides with acrylic acid efficiently without an inert atmosphere. In addition, the novel catalyst can be conveniently recovered by applying an external magnet and reused at least five times without significant loss of its activity.

© 2010 Qiu Yu Zhang. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Macroporous magnetic microspheres; Heterogeneous catalyst; Heck reaction; Palladium; Suspension polymerization

The palladium catalyzed Heck reaction has been received considerable attention in recent years, as it is an excellent method for synthesis of various organic molecules under mild conditions [1-5]. Palladium compounds such as PdCl₂, Pd(OAc)₂ and Pd(PPh₃)₄ have been widely used for this reaction as homogeneous catalysts. However, these traditional homogeneous catalysts have several drawbacks to be resolved, such as an easy contamination of palladium species in the reaction products, difficulties in recovery and recycling the expensive homogeneous palladium catalyst, which have so far limited their widespread industrial application to a large extent [6–10].

These problems can be minimized by the immobilization of homogeneous catalysts on various support materials, such as organic polymers, biopolymer, inorganic silica and other metal oxides [11–16]. This is because heterogeneous catalysts have fewer of the drawbacks of homogeneous catalysts, such as the difficulties in recovery and regeneration. In recent years, a large variety of heterogeneous palladium catalysts have been developed for Heck reaction, which results in a remarkable extension of supporting materials such as mesoporous silicane and zeolites and polymer materials. It is demonstrated that the supporting material crucially influences the catalysts from new supporting matrix with a particular purpose to make the reaction more easily separable and recyclable.

Recently, macroporous magnetic poly(GMA) microspheres have received much attention in many fields. This is mainly ascribed that they have the following three interesting features. Firstly, macroporous magnetic poly(GMA)

* Corresponding author.

E-mail address: qyzhang@nwpu.edu.cn (Q.Y. Zhang).

^{1001-8417/\$-}see front matter © 2010 Qiu Yu Zhang. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved. doi:10.1016/j.cclet.2010.04.025



Scheme 1. Preparation macroporous Fe₃O₄/P (GMA-EGDMA-DVB) microspheres and macroporous Fe₃O₄/P (GMA-EGDMA-DVB)-Pd.

microspheres have a regular pore diameter with a wide range, which can allow passage of large molecules such as organic reactants and metal complexes through the pores to reach to the surface of the channel [18]. Secondly, they have an advantage of the presence of relative oxirane groups, which can be relatively easily modifiable to a variety of functional groups suitable for prospective immobilized of enzyme, nuclei acids and other required bimolecules [19,20]. Thirdly, macroporous magnetic poly(GMA) microspheres are usually superparamagnetic, which can allow them to be conveniently recovered and separated by using an external magnetic field [21,22]. And so far, macroporous magnetic poly(GMA) microspheres have been used frequently in many fields such as wastewater treatment, environmental engineering and enzyme immobilization [23–25]. However, macroporous magnetic poly(GMA) microspheres, to the best of our knowledge, have not been used as supports for palladium catalyst.

Herein, we would like to report the feasibility of using macroporous magnetic poly(GMA) microspheres for supporting homogeneous catalyst. As shown in Scheme 1, firstly, micron-sized macroporous magnetic poly(GMA-EGDMA-DVB) microspheres with epoxy groups on the surface were prepared by suspension polymerization in the presence of inert diluents and oleic acid coated magnetic Fe_3O_4 nanoparticles. Secondly, the amino groups were introduced onto the magnetic microspheres by reacting with diethylene triamine. Finally, the amino-functionalized microspheres reacted with palladium acetates. The palladium content was determined to be 3.57 wt% by atomic absorption spectroscopy (AAS).

Fig. 1 shows the image of Fe_3O_4/P (GMA-EGDMA-DVB)-Pd. As shown in Fig. 1, it can be observed that the magnetic microspheres still maintained their configuration after coordination with palladium acetates. Furthermore, the magnetic microspheres were not broken in the coordination process.

XPS is used to study not only the coordination of macromolecular ligands with metal ions but also the chemical state of palladium presenting in the supported catalysts. The XPS data for samples are listed in Table 1. It can be seen that the binding energy of N_{1s} of Fe₃O₄/P (GMA-EGDMA-DVB)-NH₂ is 399.6 eV, which is lower than the binding energy of N_{1s} of Fe₃O₄/P (GMA-EGDMA-DVB)-Pd. Meanwhile, the binding energy of Pd_{3d5/2} in the supported



Fig. 1. SEM micrograph of Fe₃O₄/P (GMA-EGDMA-DVB)-Pd.

Table 1		
XPS data	for	samples.

Samples	Binding energy/(eV ^a)	
	Pd _{3d5/2}	N _{1s}
Pd(OAc) ₂	338.7	-
Fe ₃ O ₄ /P (GMA-EGDMA-DVB)-NH ₂	-	399.6
Fe ₃ O ₄ /P (GMA-EGDMA-DVB)-Pd	336.2	400.2

^a All relative to $C_{1s} = 284.6 \text{ eV}.$



Fig. 2. The magnetization curves measured at room temperature for Fe_3O_4/P (GMA-EGDMA-DVB)-Pd.

catalyst is 336.2 eV, which is almost similar to the binding energy of the $Pd_{3d5/2}$ of $Pd(OAc)_2$. These results indicate that coordination between N and Pd is formed in the polymer supported palladium.

Fig. 2 shows the magnetization curve of the novel catalyst at room temperature. It can be observed that the magnetization curve exhibits typical ferromagnetic behavior. Saturation of the magnetization was found to be 8.64 emu/g at an external filed of 10 kOe. With such high magnetization value, the magnetic supported catalyst can be easily separated form the solutions by using a relatively low external magnetic field.

In order to confirm whether the macroporous magnetic microspheres still maintained their mesostructure after coordination with palladium acetates, the macroporous microspheres were subsequently determined by using N₂ adsorption at 77 K. And Table 2 listed some typical pore parameters of the samples. As shown in Table 2, it can be seen that the specific surface area, pore volume and pore size of the Fe₃O₄/P (GMA-EGDMA-DVB)-Pd slightly decreased in comparison to the Fe₃O₄/P (GMA-EGDMA-DVB), which corresponds to relatively low amount of palladium particles deposited. Nevertheless, the catalyst still had a surface area of 61.7 m² g⁻¹ and a pore size diameter of 13.2 nm. These results indicate that Fe₃O₄/P (GMA-EGDMA-DVB)-Pd still preserve mesostructure and mesopores

Table 2			
Pore properties	of	sam	ples ^a .

Samples ^b	$S_{\text{BET}} (\text{m}^2 \text{g}^{-1})$	$Vp (cm^3 g^{-1})$	Pore size (nm)
1	64.5	0.22	13.7
2	63.8	0.20	13.4
3	61.7	0.21	13.2

^a Given by N₂ sorption at 77 K.

^b 1: Fe₃O₄/P (GMA-EGDMA-DVB); 2: Fe₃O₄/P (GMA-EGDMA-DVB)-NH₂; 3: Fe₃O₄/P (GMA-EGDMA-DVB)-Pd.

1064



Scheme 2. Heck reaction of aryl halide with acrylic acid catalyzed by Fe₃O₄/P (GMA-EGDMA-DVB)-Pd.

well after coordination with palladium acetates, which can allow passage of large molecules through to the pores to reach to the surface of the channel.

Furthermore, the catalytic properties of the novel magnetic catalyst for the reactions of various aryl halides with acrylic acid were also examined (Scheme 2). The results are listed in Table 3. It can be seen from the table that the Heck reactions of aryl iodides with acrylic acid can be efficiently carried out at 90 °C to afford the *trans*-product in high yields and no *cis*-product was observed. Due to the high reactivity of the aryl iodides, neither electron-donating group (entries 2–3) nor electron-withdrawing group (entries 4–5) has much influence on the yields of product. As for bromobenzene, no corresponding product (entry 6) was detected under the same reaction condition as iodobenzene. While the moderate yield (entry 7) was obtained when the reaction time extended to 10 h and the reaction temperature increased to 140 °C. It can also be seen that the reactivity of aryl bromides with electron-withdrawing substituents (entry 9) was higher than that of aryl bromides with electron-donating substituents (entry 8).

For the practical application in the Heck reaction, the lifetime of heterogeneous catalysts and their reusability are also very important factors. Thus, in order to check the recycling efficiency of the novel magnetic supported catalyst, the Heck reaction of acrylic acid with iodobenzene was investigated. After a reaction, the magnetic catalyst can be easily recovered and separated by using an external magnet, washed with ethanol and reused directly in next reaction of acrylic acid with iodobenzene without further purification. As indicated in Table 4, the novel catalyst can be reused at least five times only with a slight loss of its activity for the Heck reaction. Less than 0.1 wt% Pd leaching into the products was observed. Meanwhile, from the SEM of the supported magnetic catalyst after fifth run, we did not observe much change compared to the fresh catalyst (see Supporting information). All these results show that the novel magnetic catalyst is an excellent potential candidate for reusable and recoverable catalyst.

Entry	R	Х	Time (h)	$T(^{\circ}C)$	Yield (%) ^b
1	Н	Ι	2	90	97.6
2	OCH ₃	Ι	2	90	92.2
3	CH ₃	Ι	2	90	92.0
4	Cl	Ι	2	90	93.5
5	NO_2	Ι	2	90	98.5
6	Н	Br	2	90	0.0
7	Н	Br	10	140	52.8
8	CH ₃	Br	10	140	45.6
9	NO_2	Br	10	140	91.5

Heck reactions of various aryl halides and acrylic acid catalyzed by the magnetic catalyst^a.

^a Reaction conditions: aryl halide (5 mmol), AA (7.5 mmol), Bu₃N (10 mmol), and DMF (5 mL). Catalyst (0.3 mol% Pd) in the air.

^b HPLC yield based aryl halide.

Table 3

Table 4			
Catalyst	recycling	experiments ^a .	

Run	Time (h)	Yield (%) ^b
1	2	97.6
2	2	98.2
3	2	96.5
4	2	95.4
5	3	92.5

^a Reaction conditions: aryl halide (5 mmol), AA (7.5 mmol), Bu₃N (10 mmol), and DMF (5 mL). Catalyst (0.3 mol% Pd) in the air at 90 °C. ^b HPLC yield based aryl halide. In conclusion, we have developed a novel magnetic catalyst system composed of palladium catalyst immobilized on the backbone of macroporous magnetic microspheres prepared by suspension polymerization. The novel catalyst shows high activity in promoting Heck reaction of aryl iodides and acrylic acid. Additionally, the novel catalyst can be easily recovered and separated by using an external magnet and reused at least five times with a slight loss of its activity for the Heck reaction of iodobenzene with acrylic acid.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2010.04.025.

References

- [1] R.F. Heck, Org. React. 27 (1982) 345.
- [2] P. Beleskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009.
- [3] B.M. Bhanage, M. Arai, Catal. Rev. 43 (2001) 315.
- [4] R.B. Bedford, Chem. Commun. 20 (2003) 1787.
- [5] A.F. Littke, G.C. Fu, Angew. Chem. Int. Ed. 41 (2002) 4176.
- [6] M.A. Yamada, K. Takeda, H. Takahashi, Tetrahedron 60 (2004) 4097.
- [7] J.H. Clark, D.J. Macquarries, Green Chem. 2 (2000) 53.
- [8] S. Fujita, J. Org. Met. Chem. 687 (2003) 211.
- [9] Y.C. Cui, L. Zhang, J. Mol. Catal. A: Chem. 237 (2005) 120.
- [10] H. Mahdavi, A. Zirakzadeh, J. Amani, React. Funct. Polym. 67 (2007) 716.
- [11] T.J. Yoon, W. Lee, Y.S. Oh, New J. Chem. 27 (2003) 227.
- [12] G.F. Liu, M.Z. Cai, Catal Commun. 8 (2007) 251.
- [13] A. Dahan, M. Portnoy, Org. Lett. 5 (2003) 1197.
- [14] K. Lin, M. Song, D. Cai, Tetrahedron 44 (2003) 3955.
- [15] P. Mehnert, D.W. Weaver, J.Y. Ying, J. Am. Chem. Soc. 120 (1998) 12289.
- [16] P. Liu, Y.H. Yang, Y. Liu, et al. React. Funct. Polym. 68 (2008) 384.
- [17] C.F. Yao, H.G. Li, H.H. Wu, Catal. Commun. 10 (2009) 1099.
- [18] A. Bukowska, W. Bukowsi, J. Noworol, J. Appl. Polym. Sci. 26 (2007) 509.
- [19] D. Horak, E. Pollert, M. Trchova, Eur. Polym. J. 45 (2009) 1009.
- [20] C. Mateo, O. Abian, R. Fernadez-lifinete, Enzyme Microb. Technol. 26 (2000) 509.
- [21] C. Zhang, X. Li, J. Pang, J. Appl. Polym. Sci. 82 (2001) 1587.
- [22] S. Cakmeik, M. Gumusderedioglu, A. Denizili, React. Funct. Polym. 69 (2009) 586.
- [23] A.M. Donia, A.A. Atia, H. El-Boraey, Sep. Purif. Technol. 49 (2006) 64.
- [24] M.D. Ahmed, A.A. Asem, M.M. Ewais, Hydrometallurgy 95 (2009) 183.
- [25] P. Xue, H.F. Liu, J.H. Yan, J. Chem. Ind. Eng. 59 (2008) 443 (in Chinese).