

Chitosan-immobilized Palladium Complex: a Green and Highly Active Heterogeneous Catalyst for Heck Reaction

Pu LIU*, Lan WANG, Xiang Yu WANG

Department of Chemistry, Zhengzhou University, Zhengzhou 450052

Abstract: A green heterogeneous catalyst for Heck reaction—chitosan-immobilized palladium complex was prepared. The catalyst exhibits high activity and stereoselectivity under the moderate reaction conditions. The catalyst can be separated easily from the reaction mixture and reused after washing. Under the suitable reaction conditions, the cross-coupling of iodobenzene (ArI) with acrylic acid (AA) or acrylate can be achieved 93.3% or 99% yield of *trans*-cinnamic acid or *trans*-cinnamic ester.

Keywords: Chitosan-immobilized palladium complex, green catalyst, Heck reaction.

Heck reaction, a palladium-catalyzed carbon-carbon bond formation between aryl halides and olefins, have become an excellent tool for the synthesis of elaborated styrene derivatives and attracted much research interest in the past few years. The development of new highly active soluble Pd complexes allowed the activation and conversion of aryl halides¹. To these homogeneous Heck reactions, the catalysts were difficult to separate and further processing was necessary in subsequent reactions. Few experiments addressed to the separation of the catalyst from the reaction mixture and to reuse of the catalyst. Several attempts were made concerning the separation and recovery of the palladium complexes by the use of heterogeneous palladium system². Pd on carbon, different metal oxides and sieves were found to be the suitable catalysts for Heck reaction³. These catalysts could be separated from the reaction mixture and the residual palladium in the products could be eliminated. But the recovery of palladium from the waste catalysts was still difficult. Polymer-supported Pd complexes were also used for Heck reaction by several groups⁴. The advantage of these catalysts is that the recovery of palladium from the waste catalysts is easier. But the preparation of this kind of catalyst was rather complicated. Consequently, the development of new polymer supported catalysts is desired. These new catalysts may be friendly to the environment, have a high activity, and can be prepared easily. Chitosan is a natural polymer, contains -NH₂ group and shows a good coordination ability. Chitosan and its derivatives have attracted many attentions recently as polymeric supports in various fields, such as enzyme and metal ions immobilization, cell encapsulation, and drug deliver system.

* E-mail: liupu@zzu.edu.cn

The chitosan-immobilized metals used as catalysts for the Heck reaction has not been reported. Our interests are to examine the possibility of the immobilization of palladium on chitosan to form polymeric catalysts for the Heck reaction. In this paper, we report the results of our investigations.

Chitosan-immobilized palladium catalyst was prepared as follows: stirring 172 mL ethanol solution of PdCl₂ (concentration: 0.00893 mmol/mL) with 8 g chitosan (degree of deacetylation was more than 92%) in flask for 72 hours at room temperature, the yellow solid was then filtered and washed fully with ethanol; the yellow powder was suspended in ethanol and refluxed for 4~6 hours under nitrogen atmosphere, then the solid was dried for 24 hours at 50 °C in vacuum. Palladium content in the catalyst was 2.0 wt. %.

Table 1 Results on the Heck arylation of ArI / AA catalyzed by chitosan-immobilized palladium complex

Molar ratio of ArI / AA	Base (mmol)	Solvent	T (°C)	Time (h)	Catalyst (g)	Yield (%)
1:1	Et ₃ N (23.5)	DMF	80	5	0.2	82.3
1:1.5	Et ₃ N (23.5)	DMF	80	5	0.2	90.1
1:1.5	Et ₃ N (0)	DMF	80	5	0.2	0
1:1.5	Et ₃ N (25)	DMF	80	5	0.2	93.7
1:1.5	Et ₃ N (66)	DMF	80	5	0.2	78.4
1:1.5	Et ₃ N (25)	1,4-dioxane	80	5	0.2	74.9
1:1.5	Et ₃ N (25)	Ethanol	80	5	0.2	91.9
1:1.5	Et ₃ N (25)	H ₂ O	80	5	0.2	1.6
1:1.5	Tributylamine (25)	DMF	80	5	0.2	82.5
1:1.5	Pyridine (25)	DMF	80	5	0.2	0
1:1.5	Et ₃ N (25)	DMF	70	5	0.2	91.6
1:1.5	Et ₃ N (25)	DMF	90	5	0.2	88.2
1:1.5	Et ₃ N (25)	DMF	80	5	0.1	94.1
1:1.5	Et ₃ N (25)	DMF	80	5	0.02	82.2
1:1.5	Et ₃ N (25)	DMF	80	5	0.05	93.3
1:1.5	Et ₃ N (25)	DMF	80	4	0.05	92.7
1:1.5	Et ₃ N (25)	DMF	80	6	0.05	89.9

The typical procedure for Heck reaction is as the same as reported in literature^{3f}. The product configuration is characterized by IR and ¹HNMR spectra.

The effects of reaction factors on the yields are summarized in **Table 1**. The results showed that the optimal reaction conditions are: 10 mmol ArI, 1:1.5 molar ratio of ArI / AA, 25 mmol Et₃N, 0.05 g chitosan-immobilized palladium catalyst, 6 mL DMF, 80 °C for 5 hours. Under the above conditions, the cross-coupling of iodobenzene with acrylic acid can be achieved 93.3% yield of *trans*-cinnamic acid.

After separation and washing with DMF, the catalyst can be reused several times under the optimal reaction conditions. The results are presented in **Table 2**.

In the Heck reaction with chitosan-immobilized palladium catalyst, bromobenzene reacts much more slowly than iodobenzene does, and only trace product is obtained. As for the reaction of iodobenzene with methyl, ethyl and butyl acrylate, activity of the catalyst is high. Under the reaction conditions: 5 mmol ArI, 1:1 molar ratio of ArI and

Table 2 Heck reaction of iodobenzene with acrylic acid catalyzed by recovered catalyst

Entry	Yield (%)
fresh	93.3
1	90.0
2	89.7

acrylate, 9 mmol Et₃N, 0.1 g catalyst, 3 mL DMF, 140 °C for 8 hours, 99% yield of methyl, ethyl and butyl cinnamate can be achieved respectively.

In conclusion, we have prepared a new and green heterogeneous catalyst chitosan-immobilized palladium complex for Heck reaction. The catalyst not only has high activity but has highly stereoselective in the olefination of iodobenzene. It offers the practical advantages, such as easy preparation, separation from the reaction mixture and reuse.

Acknowledgments

This work was supported by the Youth Key Teacher Foundation from the Education Department of Henan Province (2001).

References

1. I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.*, **2000**, *100*, 3009.
2. Y. I. Ermakov, L. N. Aezamaskova, *Stud. Surf. Sci. Catal.*, **1986**, *27*, 459.
3. (a) B. M. Choudary, R. M. Sarma, K. K. Rao, *Tetrahedron*, **1992**, *48*, 719.
(b) R. L. Augustine, S. T. O'Leary, *J. Mol. Catal. A: Chem.*, **1995**, *95*, 277.
(c) A. Wali, S. M. Pillai, V. K. Kaushik, S. Satish, *Appl. Catal. A: Gen.*, **1996**, *135*, 83.
(d) F. Zhao, B. M. Bhanage, M. Shirai, M. Arai, *Chem. Eur. J.*, **2000**, *6*, 843.
(e) M. Wagner, K. Kohler, L. Djakovitch, *et al.*, *Top. Catal.*, **2000**, *13*, 319.
(f) J. M. Zhou, R. X. Zhou, L. Y. Mo, *et al.*, *Chinese J. Chem.*, **2001**, *19*, 987.
4. (a) J. Schwarz, V. P. W. Bohm, M. G. Gardiner, *et al.*, *Chem. Eur. J.*, **2000**, *6*, 1773.
(b) R. S. Varma, K. P. Naicker, P. J. Liesen, *Tetrahedron Lett.*, **1999**, *40*, 439.
(c) B. M. Bhanage, M. Shirai, M. Arai, *J. Mol. Catal. A: Chem.*, **1999**, *145*, 69.

Received 31 March, 2003