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Biopolymer-metal complex wool–Pd as a highly active heterogeneous catalyst for Heck reaction in aqueous media

Shang Wu, Hengchang Ma, Xiaojie Jia, Yunmei Zhong, Ziqiang Lei *

Key Laboratory of Polymer Materials of Gansu Province, Key Laboratory of Eco-Environment-Related Polymer Materials Ministry of Education, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, People's Republic of China

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ABSTRACT

Heterogeneous palladium catalysts, a biopolymer complex wool–Pd, have been applied in water-mediated coupling reactions of aryl bromides without assistance of any phosphine ligands. The catalyst was characterized by XPS, ICP. The results showed that aryl bromides could carry out the coupling reaction with a variety of alkenes at 80 °C, in aqueous media under atmospheric condition. More importantly, the cheap catalyst is stable, which shows negligible metal leaching, and retain good activity for at least ten successive runs without any additional activation treatment. This approach would be very useful from a practical viewpoint.

1. Introduction

The Heck reaction has been proven to be one of the most important methods for carbon–carbon bond formation between aryl halides and olefins in organic chemistry. It is used in a wide variety of organic transformations and thus it now belongs to an indispensable set of palladium-catalyzed cross-coupling reactions.[1]

In the past few years, homogeneous palladium-catalyzed reaction systems have been successfully established.[2] However, most of the reaction protocols suffer from the practical problems, such as catalyst separation, catalyst recycling, and product contamination, as well as the absolute necessary of specifical ligands[3] (for instance, phosphine or *N*-heterocyclic carbine, etc). To address these problems, supported palladium on a diverse array of organic and inorganic materials, such as resins,[4] carbon,[5] metal oxides,[6] clay,[7] ordered[8] or amorphous silicates,[9] and zeolites,[10] have been developed and used to catalyze the Heck reaction. The extensive explorations of heterogeneous catalytic systems are evidenced by a great number of publications and reviews in recent years. However, for the most cases, the immobilized catalysts generally encounter diffusion limitations under the reaction conditions can be a major problem, which was due to the aggregation and agglomeration of Pd particles into less active large particles (even bulk Pd) during the reaction. So the recyclability of the heterogeneous catalysts is thus discounted.

In previous research, some natural biopolymers, such as chitosan,[11,12] cellulose,[13] wool,[14–16] etc. have been used as efficient polymer supporters in the palladium-catalyzed several important transformations. Among them, wool represents the most special one, for the reasons that the biopolymers contain numerous amino acids units, the obvious interaction and affinity between supporter-itself and some more polar reaction media render wool with more fantastic properties, such as the possibility to taking organic reactions in aqueous phase with the assistance of this hydrophilous polymer. For the wool supported palladium catalyst, the loaded palladium particles could be distributed evenly in the surface of fibers due to the structurally ordered amino acids chains, so the formation and aggregation of Pd-black could be prevented, which was regarded as the most critical problem to the performance of palladium-catalyzed conversions.

In recent years, the green combination of aqueous media and heterogeneous palladium catalyst has been investigated as a modern fashion. Water as solvent in transition-metal catalysis has many advantages for the recycling of catalyst, product recovery, also concerning safety and environmental aspects.[17–20] Uozumi and Kimura[21] reported in 2002 a study comparing the performances of various polymeric supports holding monophosphine or chelating diphosphine palladium complexes for the coupling of iodobenzene and acrylic acid in water. From the interesting research programs, what could be concerned that the amphiphilic properties brought by the polyethylene glycol chains (PEG) promote the reaction in

* Corresponding author. Tel.: +86 931 7971687; fax: +86 931 7970359; e-mail addresses: mahczju@hotmail.com (H. Ma), leizq@nwnu.edu.cn (Z. Lei).

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water, while polystyrene (PS) only resin catalysts were not catalytically active. In other words, the water solvated Heck reaction has decisive dependence on the supporters whether which are of hydrophilicity or lipophilicity.

Herein, we report an effective catalyst system composed of wool–palladium (wool–Pd) complex in aqueous media with very small amount of PEG-400 for the Heck reaction using NaOAc as a base. The present catalysis system could be carried out in a fashion that affords an easily separable catalyst for use in subsequent catalytic chemistry at least for 10 runs, and the total TONs is 178.

2. Results and discussion

2.1. Synthesis and characterization of the catalysts

Common commercial white wool was washed with distilled water and ethanol, and then cut to pieces. Subsequently, the wool pieces were treated by the mixture of $KMnO_4$ (3 g/L) and NaCl (25 g/L), and the pH was adjusted to 2.0, the mixture was stirred at 45 °C about 45 min, and then wool was turned to black-brown. Whereafter, the black-brown wool was dipped in the solution of Na_2SO_3 (20 g/L) and HAc (10 mol/L), stirred at 50 °C for 10 min, after the wool was returned to white, washed with water several times, and then dried at 80 °C (a, Scheme 1). 1.0 g of treated-wool pieces, 2.25 mmol $PdCl_2$ were dissolved in 30 mL of de-ionized water, the mixture was stirred at room temperature for 8 h to cause white wool pieces to become brown and the solution to become colorless and transparent (b, Scheme 1). Then, the product was filtered and washed with de-ionized water(3×20 mL) and acetone (3×20 mL), dried in a vacuum oven at 60 °C for 4 h to obtain wool supported palladium complex (c, Scheme 1).

Table 1
XPS date of the wool, wool–Pd complex, and salt $PdCl_2$

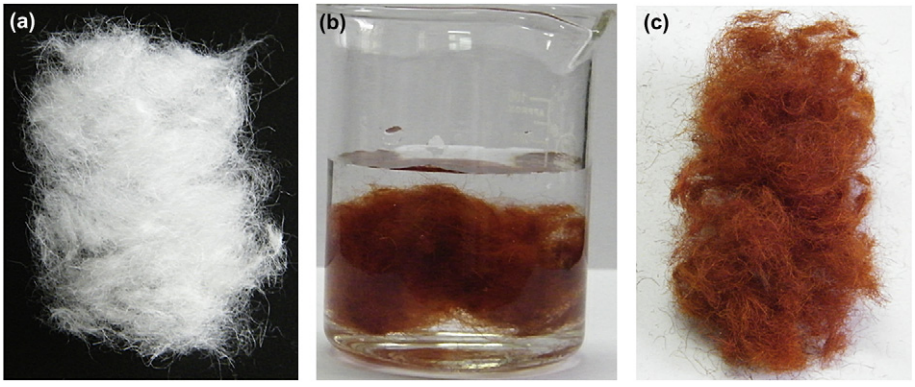
XPSPeaks		Binding energy (eV)			ΔE_b(eV)
		$PdCl_2$	Wool	Wool–Pd complex	
Pd_{3d}	$Pd_{3d\ 3/2}$	342.80		343.55	+0.75
	$Pd_{3d\ 5/2}$	337.43		338.30	+0.87
	Cl_{2p}	198.55		198.80	+0.25
N_{1s}	–NH–CO–		400.05	399.8	−0.32
	$-NH_2$		400.37	399.25	−0.55
S_{2p}	$-SO_3H$		168.18	167.87	−0.31
	–S–S–		165.05	165.75	+0.7
	–SH		163.80	163.00	−0.8
O_{1s}			531.93	532.12	+0.19

The binding energy is referred to C_{1s}=284.80 eV.

between –S–S– in wool and –S–S– in wool–Pd is 0.7 eV. The difference of O_{1s} binding energy between wool and wool–Pd also could not be detected. These results show that coordination or ionic bonds are formed by the connection of N atoms (in $-NH_2$) and S atoms (in –SH and –S–S–) with Pd atoms in the wool–Pd complex. The structure of wool–Pd may be shown as Scheme 2.

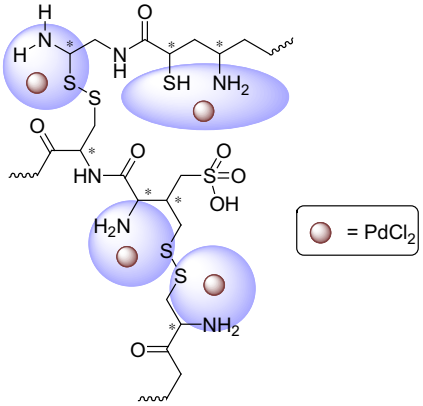
2.2. Heck reaction in water

To explore the catalytic activity of wool–Pd complex catalyst, we chose the coupling of bromobenzene with styrene as model reaction. In our catalysis system, it was observed clearly that base plays very important role in the transformation. We found that Cs_2CO_3, TBAB, Et_3N, and KOH were ineffective in providing the corresponding cross-coupling product. However, an increase in the cross-coupling reactivity was detected with Na_2CO_3 and K_2CO_3, under similar conditions. Finally, the reaction carried out in the



Scheme 1. Preparation of the wool–Pd complex.

The binding energies of wool, $PdCl_2$, and wool–Pd complex were obtained by XPS analysis (Table 1). The binding energy of the $Pd_{3d\ 3/2}$ and $Pd_{3d\ 5/2}$ in the Wool–Pd complex increase 0.75 eV and 0.87 eV, respectively; the change of Pd_{3d} binding energy means the decrease of its electron density. Little change of the binding energy of the Cl_{2p} was observed, this means there are uncreative Cl exist though the chemical bond formed in this process. There are two kinds of nitrogen-containing group; –NH–CO– and $-NH_2$ in wool, and N_{1s} binding energy for them are different. Such data in wool–Pd are also different from those in wool. The difference of N_{1s} binding energies between –NH–CO– in wool and –NH–CO– in wool–Pd is 0.32 eV, and that between $-NH_2$ in wool and $-NH_2$ in wool–Pd is 0.55 eV. In the same way, there are three kinds of S containing group, $-SO_3H$, –SH, and –S–S–, in wool, and their S_{2p} binding energies are different. The difference of S_{2p} binding energy between $-SO_3H$ in wool and $-SO_3H$ in wool–Pd is only 0.31 eV, that between –SH in wool and –SH in wool–Pd is 0.8 eV, and that



Scheme 2. The possible structure of wool–Pd.[16]