Catalytic Performance of Cellulose Supported Palladium Complex for Heck Reaction in Water

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Received 5 October 2007; accepted 29 March 2008
DOI 10.1002/app.28655
Published online 4 September 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Cellulose supported palladium complex was synthesized and characterized by XPS, TG/DTA etc. The complex was found to be an efficient catalyst for Heck reaction of acrylic acid or styrene with aryl iodides at low temperature in water under atmospheric condition, the substituted *trans*-cinnamic acid or 1,2-stilbene was obtained in stereoselectivity. Repeated tests showed that the catalyst have good reusability. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2996–3000, 2008

Key words: metal-polymer complexes; catalysts; recycling; cellulose; Heck reaction

INTRODUCTION

The palladium-catalyzed cross-coupling of aryl halides with olefins is well known as Heck reaction[1] and has been used widely in the synthesis of cinnamate derivates and pharmaceutical intermediates. Palladium complex such as $Pd(OAc_2)$ or $Pd(Ph_3)_2Cl_2$ was usually used as the catalyst for Heck reaction. Nevertheless, Pd-black often formed in the reaction process. The catalytic activity decreased and the products were polluted at the same time. In addition, the separation of the catalyst from the reaction mixture was so difficult that the recovery was impossible. The disadvantages of these homogeneous catalytic systems have precluded the widespread industrial application of Heck reaction. In recent years, the applications of polymer-supported palladium complexes for Heck reaction have been attracted considerable attention.[2–4] Many new researches and good results have been reported by Schwarz et al.,[5] Lin and Luo,[6] Bergbreiter,[7] Uozumi and Kimura[8] and Cai et al.[9–11] in this field. However, the preparations of the polymer supported palladium catalysts involve many steps because most of the carriers employed are synthetic polymers, and the cost of the catalyst was high.

Cellulose is the most abundant natural polymer in the world. It is the most important structural material in higher plants, and the weigh of cellulose takes up more than 1/3 of the whole one. In addition, cellulose also exists in protozoa, alga, and bacteria. Cellulose is the condensation product of β-D-pyran glucose with no branched chains. With the rapid development of modern science and technology, cellulose and its derivates were applied widely in the areas such as pesticide, cosmetic'grocery, medicine, petroleum drilling, paper making, textile etc since the middle period of 20 century.[12]

Cellulose is a natural polymer with abundant hydroxyl groups existing in the molecular structure. Palladium can be loaded on the cellulose through the interaction of hydroxyl groups with palladium atoms. There are very few reports on Heck reaction catalyzed by natural polymer supported palladium complexes. Macquarrie and coworkers[13] reported that 2-pyridinecarboxaldehyde modified chitosan supported palladium complex was an active catalyst for Heck reaction. Reddy et al.[14] reported the catalysis of cellulose supported palladium(0) catalyst for Heck and Sonogashira coupling reactions in organic solvent. The yields of the product were high but required long reaction time and high reaction temperature. Recently, we also reported the catalytic activity of chitosan derivatives supported palladium complexes for Heck arylations.[15] In this article, cellulose supported palladium complex was synthesized easily and characterized by XPS, TG/DTA etc. The complex exhibited high activity for Heck reaction of acrylic acid or styrene with aryl iodides in water at low temperature under atmospheric condition, the substituted *trans*-cinnamic acid or 1,2-stilbene was obtained in stereoselectivity.

EXPERIMENTAL

Materials and equipment

X-ray photoelectron spectra (XPS) were measured on an AXISULTRA spectrometer (Kratos Company, England) using mono-Al Ka radition. The C_{1s}

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TABLE I
XPS data of Pd, $PdCl_2$, Cellulose, and Cellulose Supported Palladium Catalyst (eV[a])

Samples	Pd	$PdCl_2$	Cellulose	Cellulose supported palladium catalyst
$Pd_{3d5/2}$	335.4	338.3		335.7, 337.6
O_{1s}			531.2	531.6

[a] All relative to $C_{1s} = 284.8$ eV.

photoelectron line was used for energy calibration and the C_{1s} binding energy was taken to be 284.8 eV. The thermal analysis was performed on an EXSTAR6000 (Seiko Company, Japan) thermal analysis system at a heating rate of 10°C/min in the air.

Cellulose (industrial grade); palladium chloride (analytical pure); iodobenzene, *p*-iodoanisole (98%), *p*-iodobenzoic acid (98%), 1-iodo-4-chlorobenzene (98%) were obtained from Lancaster and used as received; Acrylic acid, styrene were analytical reagents and were distilled before use. All other reagents were analytical pure and used as received.

Preparation of cellulose supported palladium complex

Cellulose (2.0 g) and $PdCl_2$ (0.3 g) was added to ethanol (50 mL). The mixture was stirred at 60°C in the air for 72 h. After the reaction mixture was cooled to room temperature, it was filtered and washed with acetone (3 × 20 mL) and H_2O (3 × 20 mL) and then dried at 100°C in vacuum for 6 h to give 2.0 g of cellulose supported palladium complex.

Typical procedure for the Heck arylation of aryl iodides with acrylic acid

Certain amount of cellulose supported palladium complex, acrylic acid (3.3 mmol), iodoarene (3.0 mmol), tributylamine (6.6 mmol), and H_2O (0.5 mL) were added to a round bottomed flask and stirred at proper temperature in the air for 2 h. After the reaction mixture was cooled to room temperature, H_2O (15 mL) and Na_2CO_3 (0.5 g) were added. After stirring for 10 min, cellulose supported palladium complex was separated by filtration, washed with H_2O (2 × 15 mL), EtOH (2 × 15 mL), and Et_2O (2 × 15 mL). The filtrate was treated with 3*N* HCl (5 mL) and lots of white precipitate was appeared immediately. The precipitate was filtered, washed with H_2O (2 × 15 mL) and dried in the air to give the product. The product was characterized by ^{1}H-NMR and IR.

Typical procedure for the Heck arylation of aryl iodides with styrene

Certain amount of cellulose supported palladium complex, styrene (3.3 mmol), aryl iodides (3.0 mmol), tributylamine (3.3 mmol), and H_2O (0.5 mL) were added to a round bottomed flask and stirred at proper temperature in the air for 2 h. The mixture was cooled to room temperature and dissolved in Et_2O (30 mL). Cellulose supported palladium complex was recovered from the mixture by filtration, washed with H_2O (2 × 15 mL), EtOH (2 × 15 mL), and Et_2O (2 × 15 mL). The filtrate was treated with 3*N* HCl (2 × 15 mL), brine (3 × 15 mL) and dried over $MgSO_4$. The solid product was obtained by recrystallization from Et_2O to give *trans*-stilbene. The product was characterized by H^1 NMR and IR.

RESULTS AND DISCUSSION

Characterization of cellulose supported palladium complex

Cellulose is a natural polymer with abundant hydroxyl groups existing in the molecular structure. Palladium can be loaded on the cellulose through the interaction of hydroxyl groups with palladium. The binding energies of Pd, $PdCl_2$, cellulose, and cellulose supported palladium complex were obtained by XPS analysis. The results were summarized in Table I. The binding energies of $Pd_{3d5/2}$ in PVC-EN-Pd are 335.7 and 337.6. The fact shows that two different chemical state of Palladium (Pd^0 and pd^{2+}) exists. The binding energy of O_{1s} in cellulose supported palladium catalyst is 531.6 eV and it is higher

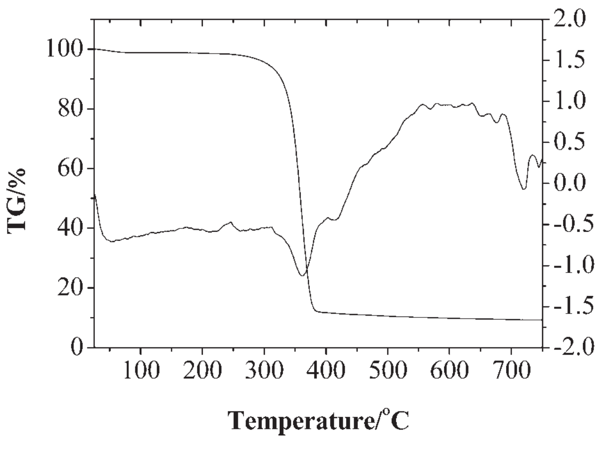


Figure 1 TG and DTA curves of cellulose supported palladium catalyst.

TABLE II
Effect of the Solvent on the Catalyst Performance[a]

Entry	Solvent	Time/h	Yield[b]/%
1	NMP	5	78.2
2	DMF	5	86.1
3	ethanol	5	83.5
4	DMSO	5	88.2
5	H_2O	5	92.8

[a] Reaction condition: iodobenzene 3.3 mmol, acrylic acid 3.0 mmol, tributylamine 3.3 mmol and solvent 0.5 mL at 90°C in the air.
[b] Isolated yield was based on the iodobenzene.

TABLE IV
Effect of Amount of Catalyst on Catalytic Performance[a]

Entry	x(Pd)/mol%	Time/h	Yield[b]/%
1	0.5	5	90.0
2	0.25	5	93.0
3	0.125	5	92.8
4	0.05	6	82.6
5	0.025	12	68.0

[a] Reaction condition: iodobenzene 3.3 mmol, acrylic acid 3.0 mmol, tributylamine 3.3 mmol and H_2O 0.5 mL at 90°C in the air.
[b] Isolated yield was based on the iodobenzene.

than that in cellulose, which indicates the coordination of O with Pd^0 or pd^{2+} are formed.

Thermal stability of the catalyst has great effect on its catalytic activity and recyclability because Heck reaction is usually carried out at high temperature. The TG and DTA curves of cellulose supported palladium complex were shown as Figure 1. It can be found that cellulose supported palladium complex was stable up to 260°C. Weight loss along with exothermic peak appeared when the temperature was higher than 260°C. With the temperature enhanced continuously, cellulose supported palladium complex decomposed gradually, and the weight loss was more and more obvious. The decomposition of the cellulose supported palladium complex was complete when the temperature was raised to 375°C and the oxide of palladium was left.

Effect of the solvent on the catalytic performance

The Heck reaction was usually carried out in the organic solvent because the oil-solubility of the substrate. It is well known that the large use of organic solvent caused much bad result in chemical manufacture. So it has been hoped for a long time that the organic solvent could be replaced by water in organic reactions. It is very lucky that the Heck reaction catalyzed by cellulose supported palladium catalyst was carried out efficiently in water. The research results were list in Table II. It was found from the Table IV that the Heck reaction was carried out in several different organic solvents. However, the catalytic activity of cellulose supported palladium catalyst for Heck reaction in water is higher than in the organic solvent, and the yield reached 92.8%, which probably due to the fine dispersibility of cellulose in water. Moreover, the Heck reaction catalyzed by cellulose supported palladium catalyst was also processed successfully without inert condition, which makes it very practical.

Effect of temperature on catalytic performance

The catalytic activity of the supported palladium complex for Heck reaction varied markedly at the different temperature. The effect was studied by using Heck arylation of acrylic acid and iodobenzene with 0.25 mol % amount of the catalyst and the results were listed in Table III. The reaction catalyzed by cellulose supported palladium complex processed successfully even at the low temperature as 60°C and the yield exceeded 80%. The yield of the product increased and the reaction time decreased on condition that the reaction temperature was raised from 60 to 90°C. The yield of the product decreased slightly at higher temperature probably due to the increasing side reactions. Compared with the result of Hardy's research[13] on the Heck reaction of iodobenzene and butyl acrylate catalyzed by chitosan supported

TABLE III
Effect of the Reaction Temperature on Catalytic Performance[a]

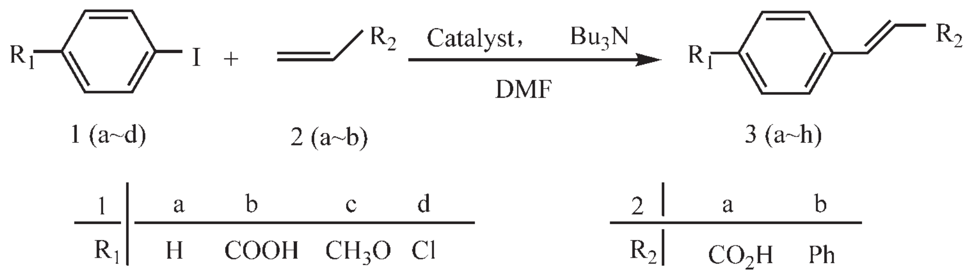
Entry	Temp./(°C)	Time/h	Yield[b]/%
1	60	5.5	81.0
2	80	5.5	82.2
3	90	5	92.8
4	100	5	88.0
5	110	5	86.1

[a] Reaction condition: iodobenzene 3.3 mmol, acrylic acid 3.0 mmol, tributylamine 3.3 mmol, and H_2O 0.5 mL in the air.
[b] Isolated yield was based on the iodobenzene.

TABLE V
Effect of Tie-Acid Agent on Catalytic Performance[a]

Entry	Tie-acid agent	Time/h	Yield[b]/%
1	$N(Et)_3$	5	83.2
2	$N(t\text{-}Bu)_3$	5	92.8
3	pyridine	5	13.6
4	NaOAc	5	0
5	NaOH	5	0

[a] Reaction condition: iodobenzene 3.3 mmol, acrylic acid 3.0 mmol, tie-acid agent 3.3 mmol and H_2O 0.5 mL at 90°C in the air.
[b] Isolated yield was based on the iodobenzene.



Scheme 1 Heck reaction catalyzed by cellulose supported palladium catalyst.

palladium complex, the cellulose supported palladium complex showed higher activity even at lower temperature with shorter reaction time.

Effect of amount of catalyst on catalytic performance

The effect of amount of catalyst on catalytic property is an important factor to estimate the value of the catalyst because palladium is an expensive metal. The effect was studied by using Heck arylation of acrylic acid with iodobenzene at 90°C and the results were summarized in Table IV. The reaction can be carried out efficiently with tiny amount of the catalyst (0.025 mol % Pd), and the yield of the cinnamic acid was 68%. Increasing the amount of the catalyst, the yield of the product enhanced and the reaction time decreased. Nevertheless, the yield of the product and the reaction time changed slightly after the amount of the catalyst was increased to 0.125 mol % Pd.

Effect of the tie-acid agent on catalytic performance

The effect of different tie-acid agents on catalytic activity of cellulose supported palladium complex was also investigated in water at 90°C with amount of catalyst was 0.125 mol %Pd (Table V). The yield of the product was high when the strong organic alkali was adopted as the tie-acid agent. On the other hand, the catalytic activity of the complex was lost in the presence of inorganic alkali.

Heck arylations of aryl iodides with alkenes catalyzed by cellulose supported palladium catalyst

Cellulose supported palladium complex was further evaluated in Heck arylations (Scheme 1) of iodoarenes with acrylic acid or styrene under similar condition. As seen from Table VI, the Heck arylations of acrylic acid or styrene with aryl iodides were processed efficiently and the trans-products were obtained in high yield. IR and ^{1}H-NMR spectra of all products were conformed. Neither electron-donating group nor electron-withdrawing group on aryl iodides has much effect on the yield of products. The results indicated that the cellulose supported palladium complex was a novel efficient catalyst for Heck reaction.

Reusability of cellulose supported palladium complex

The catalysts can be recovered easily from the reaction mixture by filtration. After being washed adequately with H_2O, CH_3CH_2OH, and Et_2O and dried in the air, the catalyst was reused for Heck reaction of acrylic acid with iodobenzene in water. Repeated using the catalyst for five times, the yield

TABLE VI
Heck Arylation of Aryl Iodide with Alkene Catalyzed by Cellulose Supported Palladium Catalyst[a]

Entry	Aryl iodide	Alkene	Solvent	Time/h	Temp./°C	Product	Yield[b]/%
1	1a	2a	H_2O	5	90	3a	92.8
2	1b	2a	H_2O	5	90	3b	87.2
3	1c	2a	H_2O	5	90	3c	98.6
4	1d	2a	H_2O	5	90	3d	99.1
5	1a	2b	H_2O	6	90	3e	98.4
6	1b	2b	H_2O	6	90	3f	99.6
7	1c	2b	H_2O	6	90	3g	99.8
8	1d	2b	H_2O	6	90	3h	99.5

[a] Reaction condition: aryl iodides 3.3 mmol, acrylic acid 3.0 mmol, tributylamine 3.3 mmol and H_2O 0.5 mL at 90°C in the air.
[b] Isolated yield was based on the aryl iodide.

of the product was 92.8%, 83.3%, 80.2%, 78.6%, 76.7%, respectively, which showed the good reusability of cellulose supported palladium complex

CONCLUSIONS

Cellulose supported palladium complex was synthesized via simply method and characterized by XPS, TG/DTA etc. The Heck reaction of conjugated olefins with aryl iodides catalyzed by cellulose supported palladium complex were processed efficiently at 90°C in water under atmospheric condition, the substituted *trans*-cinnamic acid or 1,2-stilbene was obtained in stereoselectivity. The catalyst can be recycled several times for the Heck reaction and should be considered as a novel efficient catalyst for Heck reaction in water.

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