

Sesbania Gum Xanthate Supported Palladium Complex as an Efficient Catalyst for Heck Reaction

Lei Zhang, Puyu Zhang, Xiang Li, Yuanchen Cui

College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475001, China

Received 11 February 2006; accepted 21 August 2006

DOI 10.1002/app.26210

Published online 26 April 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Sesbania gum xanthate supported palladium complex (SG-CS₂-Pd) was synthesized and characterized by XPS, TGA, DTA, etc. The complex exhibits high activity and stereoselectivity for Heck reaction under atmospheric condition and can be easily recovered and reused. Heck reaction of styrene with iodobenzene can be carried out efficiently by using SG-CS₂-Pd as catalyst even at the low temperature (70°C) or with tiny amount of the catalyst (0.1 mol % Pd). SG-CS₂-Pd has high catalytic activity for arylation of acrylic acid or styrene with iodobenzene under

the condition of NMP as solvent and the yield of cinnamic or trans-stilbene exceeded 90%. The Heck arylation of substituted iodobenzene with acrylic acid or styrene with iodobenzene can also be efficiently catalyzed by using SG-CS₂-Pd as catalyst under the conditions of 90°C, NMP as solvent. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2198–2202, 2007

Key words: metal-polymer complexes; catalysts; recycling; heck reaction; sesbania gum

INTRODUCTION

The palladium-catalyzed cross-coupling of aryl halide with olefine is well known as Heck reaction and has become a very versatile tool in organic synthesis.¹ In this reaction, homogeneous catalytic systems have been proven to be efficient and palladium complexes such as Pd(OAc)₂ or Pd(Ph₃)₂Cl₂ were usually used as the catalyst. However, the homogeneous catalytic system suffers from severe problems associated with the separation, recovery, and the instability at high temperatures, which have so far precluded its widespread industrial application. In addition, in view of the economy of the reaction, the recovery as well as recycling of the expensive palladium catalyst is required. These problems can be overcome by the use of heterogeneous catalysts, made up of supported palladium complex, such as palladium on carbon,^{2–3} metal oxides,^{4–6} clays,^{7–9} zeolites,^{10,11} and molecular sieves,^{12,13} etc. Recently, polymer-supported palladium complexes have been attracting considerable attention because of their high activity and good recyclability. Andersson,¹⁴ Schwarz,¹⁵ Uozumi,¹⁶ and Cai^{17–19} reported a series of synthetic polymers supported palladium catalysts that showed good catalytic activity for Heck reaction.

Natural polymers or functional groups modified natural polymers are good carriers for metal. Several

groups have demonstrated the catalytic activity of chitosan-based heterogeneous catalysts in hydrogenation,^{20–22} polymerization of alkenes,²³ oxidation,^{24,25} cyclopropanation of alkenes,^{26,27} etc. The reports on Heck reaction catalyzed by natural polymer supported palladium complexes are very few presently. Hardy²⁸ reported that 2-pyridinecarboxaldehyde modified chitosan supported palladium complex was an active catalyst for Heck reaction. Recently, we also reported the catalytic activities of two kinds of chitosan derivatives supported palladium complexes for Heck arylations.²⁹ Sesbania gum (abbreviated as SG) is a kind of plant glue that is distilled from endo-albumen in sesbania legume. Sesbania gum belongs to the savageness amylose macromolecule compound ($M = 3.91 \times 10^5$), and its main component is galactomannan. In this article, we report the synthesis and characterization of sesbania gum xanthate supported palladium complex and the applications of the complex for Heck reaction. The results show that the complex is highly active for the Heck arylations of aryl iodides with acrylic acid or styrene at 90°C with tiny amount of the catalyst and can be reused many times.

EXPERIMENTAL

Materials and equipment

Acrylic acid, styrene, *N,N'*-dimethyl acetamide (DMAc), *N,N'*-dimethyl formamide (DMF), *N*-methyl pyrrolidone (NMP), Dimethyl sulfoxide (DMSO) were distilled before use. 4-iodoanise (98%), 1-iodo-

Correspondence to: Y. Cui (yccui@henu.edu.cn).

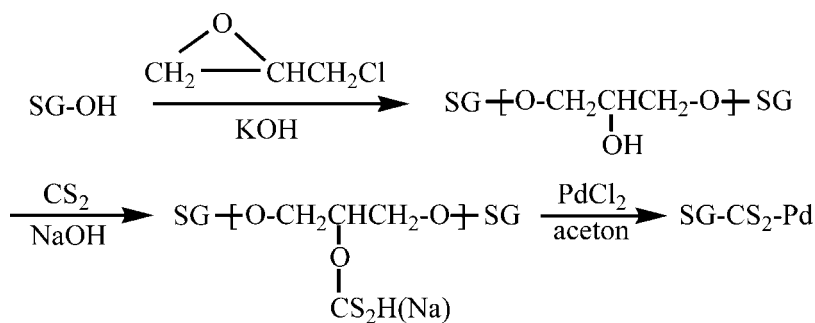


Figure 1 Synthesis route of SG-CS₂-Pd.

4-nitrobenzene (98%), 4-iodotoluene (98%), 1-iodo-4-chlorobenzene (98%) were obtained from Lancaster and used as received. All other reagents were obtained from commercial sources and used as supplied.

IR spectra were performed on an Avatar360 Fourier Transform Infrared FTIR spectroscopy (Nicolet Company, American). X-ray photoelectron spectra (XPS) were measured on an AXISULTRA spectrometer (Kratos Company, England) using mono-Al K α radiation. The C_{1s} photoelectron line was used for energy calibration and the C_{1s} binding energy was taken to be 284.8 eV. Thermal analysis was performed on an EXSTAR6000 (Seiko Company, Japan) thermal analysis system at a heating rate of 10°C/min in the air.

Preparation of the sesbania gum xanthate supported palladium complex

Sesbania gum (0.5 g) was dissolved in 5 mL 1% NaCl solution by stirring. After the mixture was heated to 45°C, 15% KOH (0.15 mL) was added, then, epoxy chloropropane (0.1 mL) was added slowly, and the mixture was stirred at 45°C. After being stirred for 8 h, H₂O (1 mL) was added to dilute the reaction mixture, then 30% NaOH (0.1 mL) and CS₂ (0.2 mL) were added. The mixture was stirred continuously at 45°C for 2 h. After the reaction was completed, 0.18 g MgSO₄ was added and stirred for 20 min. The reaction mixture was filtered and washed with water (3 × 20 mL) and ethanol (3 × 20 mL). About 0.48 g sesbania gum xanthate was obtained after being dried at 80°C in the air for 6 h. IR (KBr): $\nu(\text{cm}^{-1})$ 3427, 2929, 1651, 1451 ~ 1475, 1382, 1061, 832, 668.

PdCl₂ (0.3 g) was added to the mixture of sesbania gum xanthate (2.0 g) in acetone (50 mL). The mixture was stirred at room temperature in the air for 72 h. The reaction mixture was filtered and washed with acetone (3 × 20 mL) and H₂O (3 × 20 mL) and then dried at 80°C in vacuum for 6 h to give 2.2 g sesbania gum xanthate supported palladium complex (abbreviated as SG-CS₂-Pd) (Fig. 1).

Typical procedure for the Heck reaction of aryl iodides with styrene

SG-CS₂-Pd (0.5 mol%), styrene (2.0 mmol), aryl iodides (1.0 mmol), tributylamine (2.0 mmol), and NMP (0.5 mL) were taken in a round bottomed flask and stirred at 90°C in the air for 2 h. The mixture was dissolved in Et₂O (20 mL) after it was cooled to room temperature. SG-CS₂-Pd was recovered from the mixture by filtration, washed with H₂O (3 × 10 mL), EtOH (3 × 10 mL), and Et₂O (3 × 10 mL). The filtrate was treated with 3N HCl (3 × 10 mL), brine (3 × 10 mL), and dried over MgSO₄. The solid product was obtained by recrystallization from Et₂O to give trans-stilbene.

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

SG-CS₂-Pd (0.5 mol %), acrylic acid (2.0 mmol), iodoarenes (1.0 mmol), tributylamine (3.0 mmol), and NMP (0.5 mL) were taken in a round-bottomed flask and stirred at 90°C in the air for 2 h. After the reaction mixture was cooled to room temperature, H₂O (20 mL) and Na₂CO₃ (0.5 g) were added. After being stirred for 10 min, SG-CS₂-Pd was separated by filtration. The filtrate was treated with 3N HCl (5 mL). The precipitate was filtered, washed with H₂O (3 × 10 mL) and dried in the air to give trans-cinnamic acid.

TABLE I
XPS Data for Pd, PdCl₂, SG-CS₂, and SG-CS₂-Pd (in eV)^a

Samples	S 1s	O 1s	Pd 3d5/2
Pd			335.4
PdCl ₂			338.3
SG-CS ₂	163.7	168.6	533.4
SG-CS ₂ -Pd	163.5	168.9	534.8
			532.2
			532.9
			335.6
			337.8

^a All relative to C_{1s} = 284.8 eV.

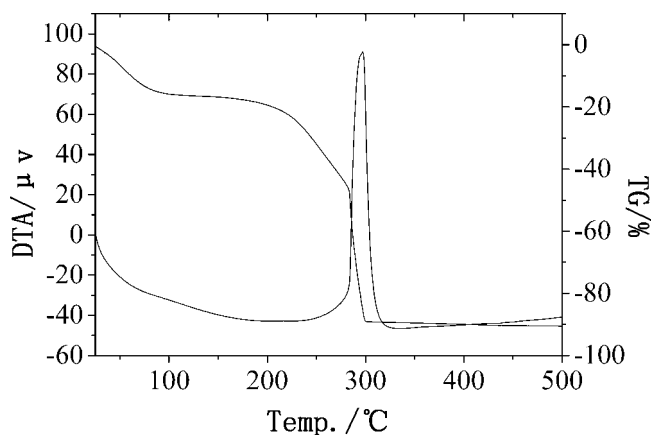


Figure 2 TGA and DTA curves of SG-CS₂-Pd.

RESULTS AND DISCUSSION

Characterization

To study the chemical states of palladium present in the supported catalyst and the coordination of macromolecular ligands with metal ions, the binding energies of Pd, PdCl₂, SG-CS₂, and SG-CS₂-Pd were obtained through the XPS analysis. The results are summarized in Table I. The binding energies of Pd 3d_{5/2} in SG-CS₂-Pd are 335.6 and 337.8, which suggests that the existence of two different chemical state of Palladium, Pd⁰ and Pd²⁺. The binding energies of O 1s in SG-CS₂-Pd have two different data (533.4, 532.2) and they are higher than those in SG-CS₂, which indicates the lone-pair electrons on the O atoms transfers and the electron cloud density at O atom decreases. The result confirms the coordination of O atoms with Pd⁰ or Pd²⁺. The binding energies of S 1s in SG-CS₂-Pd (163.7, 168.6) or SG-CS₂ (163.5, 168.9) do not have much difference, which is probably due to the counteraction between the opposite-coordination of Pd→S and the coordination of S with Pd. The similar result can also be seen from other literature.³⁰

TABLE II
Effect of Reaction Temperature
on Catalytic Performance^a

Entry	Temp/°C	Time/h	Yield ^b /%
1	100	5	99
2	90	6	98
3	80	7	95
4	70	8	88
5	70	12	93
6	60	12	80
7	60	14	84

^a Reactions were carried out with SG-CS₂-Pd (1.0 mol % Pd), iodobenzene (1.0 mmol), styrene (2.0 mmol), tributylamine (2.0 mmol), NMP (0.5 mL) in the air.

^b Isolated yield was based on the iodobenzene.

TABLE III
Effect of Amount of Catalyst on Catalytic Performance^a

Entry	Amount of Catalyst/mol % Pd	Time/h	Yield ^b /%
1	1.0	6	99
2	0.5	8	99
3	0.2	24	96
4	0.1	36	95
5	0.05	60	–

^a Reactions were carried out with proper amount of SG-CS₂-Pd, iodobenzene (1.0 mmol), styrene (2.0 mmol), tributylamine (2.0 mmol), NMP (0.5 mL) at 90°C in the air.

^b Isolated yield was based on the iodobenzene.

Thermal stability of the catalyst has a great effect on its catalytic activity and recyclability because Heck reaction is usually carried out under high temperature conditions (100°C). TGA and DTA curves of SG-CS₂-Pd under atmospheric conditions are shown in Figure 2. TGA analysis shows that SG-CS₂-Pd is stable from room temperature to 230°C. Then the fast loss of weight is observed probably due to the oxidative decomposition of the polymer ligands. Thermal analysis indicates that sesbania gum xanthate supported palladium complex meets the basic thermal qualification as an efficient supported catalyst for Heck reaction.

Catalytic performance of the SG-CS₂-Pd

Most homogeneously and heterogeneously catalyzed Heck reactions are carried out under inert condition.^{14,17–19} The Heck reaction catalyzed by SG-CS₂-Pd can be carried out efficiently in the air. Such nature of the catalyst makes it convenient in practical applications. The Heck reaction catalyzed by supported palladium complex is usually carried out at 100°C. High temperature is another important obstacle to restrict its widespread application. The influence of temperature on catalytic property of SG-CS₂-Pd was investigated by using Heck arylation of iodobenzene with styrene. It was found from the Table II that the catalytic activity of SG-CS₂-Pd remained at very high level while the temperature decreased from 100 to 80°C, and the yield of the trans-stilbene acid was above 90%. With reaction temperature reduced to 70°C, the Heck reaction could also be efficiently catalyzed by SG-CS₂-Pd under the condition of increasing reaction time. The yield of cinnamic reached 93% at 12 h. Analogous results could be observed when the reaction was carried out at 60°C. The yield of the product was 84% even if the reaction temperature was reduced to 60°C. Compared with the results of Hardy's researches²⁸ on Heck reaction of iodobenzene with butyl acrylate in 42 h at 100°C, the SG-CS₂-Pd catalyst has better performance even at low temperature with short reaction time.

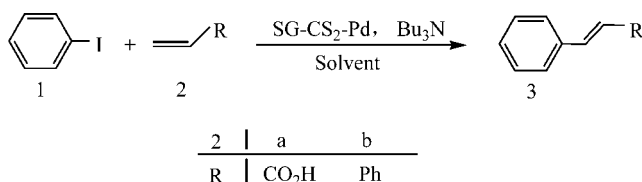


Figure 3 Heck reaction of Iodobenzene with Acrylic or Styrene catalyzed by SG-CS₂-Pd.

The effect of amount of catalyst on catalytic property is one of the important factors to estimate the value of the catalyst because palladium is an expensive metal. The effect was studied by using Heck arylation of iodobenzene with styrene and the results were summarized in Table III. With amount of catalyst ranging from 1.0 to 0.1 mol % Pd, the yield of the cinnamic acid in the Heck reaction performed by SG-CS₂-Pd did not reduce remarkably and were all above 95%. However, the reactions required long time with the amount of catalyst reduced. The results showed that the catalyst SG-CS₂-Pd has high catalytic activity with amount of catalyst ranging from 1.0 to 0.1 mol % Pd. Nevertheless, with the amount of catalyst reduced to 0.05 mol % Pd, the arylation was not carried out efficiently, and the product could hardly be observed.

The effect of solvent on catalytic property of SG-CS₂-Pd was also investigated by the use of Heck arylation (Fig. 3) of acrylic acid or styrene with iodobenzene, and the results were summarized in Table IV. NMP, ethanol, and DMF were the appropriate solvent for Heck reaction of acrylic acid with iodobenzene. The catalytic property of SG-CS₂-Pd for Heck reaction of styrene with iodobenzene was further studied with NMP, ethanol, or DMF as solvent. The yield was 99%, 95% and 84%, respectively. It was concluded that SG-CS₂-Pd has high catalytic activity under the condition of NMP as

TABLE IV
Effect of Solvent on Catalytic Performance^a

Entry	Alkenes	Solvents	Time/h	Products	Yield ^b /%
1	2a	NMP	5	3b	91
2	2a	Ethanol	5	3b	83
3	2a	DMF	5	3b	93
4	2a	DMAc	5	3b	77
5	2a	Acetone	5	3b	77
6	2a	DMSO	5	3b	71
7	2b	NMP	6	3a	99
8	2b	Ethanol	6	3a	95
9	2b	DMF	6	3a	84

^a Reactions were carried out with SG-CS₂-Pd (0.5 mol % Pd), aryl iodides (1.0 mmol), alkene (2.0 mmol), tributylamine (2.0 mmol), NMP (0.5 mL) at 90°C in the air for 3 h. When alkene was used as acrylic acid, 3.0 mmol tributylamine was added.

^b Isolated yield was based on the aryl iodides.

TABLE V
Recycling and Reuse of SG-CS₂-Pd for the Heck reaction^a

Cycle	Temp/°C	Time/h	Yield ^b /%
1	90	5	93
2	100	8	91
3	100	12	88
4	100	18	84
5	100	24	81
6	100	30	77

^a Reactions were carried out with SG-CS₂-Pd (0.5 mol % Pd), iodobenzene (1.0 mmol), acrylic acid (2.0 mmol), tributylamine (3.0 mmol), NMP (0.5 mL) in the air.

^b Isolated yield was based on the iodobenzene.

solvent, and the yield exceeded 90% for Heck reaction of acrylic acid or styrene with iodobenzene.

The catalyst could be recovered easily from the reaction mixture by filtration. After being washed with ethanol and dried in the air, the heterogeneous catalyst SG-CS₂-Pd was reused for Heck reaction. Recycling and reuse of the SG-CS₂-Pd were examined for the reaction of iodobenzene with acrylic acid. It was found from the Table V that SG-CS₂-Pd could be reused six times under the conditions of higher temperature and longer time than the first cycle. The yield of the trans-cinnamic acid was up to 77% at the sixth cycle, which indicated the high stability and good recyclability of SG-CS₂-Pd.

SG-CS₂-Pd was further evaluated in Heck arylation (Fig. 4) of iodoarenes with acrylic acid or styrene with NMP as a solvent and tributylamine as base under atmospheric condition. The results in Table VI made it clear that the Heck arylations of acrylic acid or styrene with substituted iodobenzene was carried out efficiently at 90°C to afford the trans-product in high yield, and cis-product was not observed. All the products were confirmed by IR and ¹H NMR spectra. Neither electron-donating group nor electron-withdrawing group on aryl iodides has a great effect on the yield of products. We have reported the polyvinyl chloride-polyethylene-polyamine and chitosan derivatives supported palladium complexes as efficient heterogeneous catalyst for Heck reaction. Compared with the results on Heck reaction catalyzed by organosilicon polymer supported palladium complex reported by Cai¹⁷⁻¹⁹ and our researchers^{29,31} on Heck

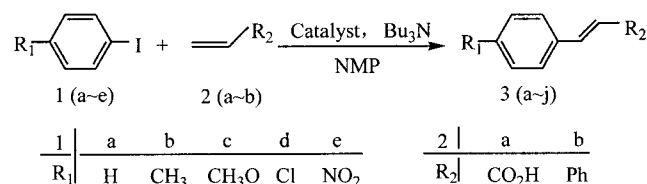


Figure 4 Heck reaction of Iodoarenes with Acrylic or Styrene catalyzed by SG-CS₂-Pd.

TABLE VI
Heck Arylation of Iodoarenes with Alkenes
Catalyzed by SG-CS₂-Pd^a

Entry	Aryl halides	Olefines	Products	Yield ^b /%
1	1a	2a	3a	98
2	1b	2a	3b	91
3	1c	2a	3c	92
4	1d	2a	3d	95
5	1e	2a	3e	97
6	2a	2b	3f	96
7	2b	2b	3g	90
8	2c	2b	3h	91
9	2d	2b	3i	93
10	2e	2b	3j	95

^a Reactions were carried out with SG-CS₂-Pd (0.5 mol % Pd), aryl iodides (1.0 mmol), alkene (2.0 mmol), tributylamine (2.0 mmol), NMP (0.5 mL) at 90°C in the air for 3 h. When alkene was used as acrylic acid, 3.0 mmol tributylamine was added.

^b Isolated yield was based on the aryl iodides.

reaction performed by polyvinyl chloride-polyethylene-polyamine and chitosan derivatives supported palladium complexes, the catalyst SG-CS₂-Pd should be considered as another new efficient heterogeneous catalyst for Heck reaction.

CONCLUSIONS

SG-CS₂-Pd has been prepared easily by using inexpensive natural polymer ligand and exhibited high activity for Heck reaction of aryl iodides with olefines even with tiny amount of the catalyst in the air. The Heck reaction could also be efficiently catalyzed by SG-CS₂-Pd at different temperature with proper reaction time. SG-CS₂-Pd exhibited high catalytic activity for Heck reaction of acrylic acid or styrene with different iodoarenes under the condition of NMP as solvent. The catalyst was separated and recovered easily from the reaction mixture by filtration and reused six times.

References

1. Heck, R. F. *Org React* 1982, 27, 345.
2. Beller, M.; Kühlein, K. *Synlett* 1995, 441.
3. Köhler, K.; Heidenreich, R. G.; Krauter, J. G. E.; Pietsch, J. *Chem Eur J* 2002, 8, 622.
4. Davies, I. W.; Matty, L.; Hughes, D. L.; Reider, P. J. *J Am Chem Soc* 2001, 123, 10139.
5. Zhao, F. Y.; Shirai, M.; Ikushima, Y.; Arai, M. *J Mol Catal A: Chem* 2002, 180, 211.
6. Pröckl, S. S.; Kleist, W.; Gruber, M. A.; Köhler, K. *Angew Chem Int Ed* 2004, 43, 1881.
7. Ramchandani, R. K.; Uphade, B. S.; Vinod, M. P.; Wakharkar, R. D.; Choudhary, V. R.; Sudalai, A. *Chem Commun* 1997, 2071.
8. Varma, R. S.; Naicker, K. P.; Liesen, P. J. *Tetrahed Lett* 1999, 40, 2075.
9. Poyatos, M.; Márquez, F.; Peris, E.; Claver, C.; Fernandez, E. *New J Chem* 2003, 27, 425.
10. Corma, A.; García, H.; Leyva, A.; Primo, A. *Appl Catal A: General* 2004, 257, 77.
11. Djakovitch, L.; Koehler, K. *J Am Chem Soc* 2001, 123, 5990.
12. Mehnert, C. P.; Weaver, D. W.; Ying, J. Y. *J Am Chem Soc* 1998, 120, 12289.
13. Venkatesan, C.; Singh, A. P. *J Catal* 2004, 227, 148.
14. Andersson, C. M.; Karabelas, K.; Hallberg, A.; Andersson, C. *J Org Chem* 1985, 50, 3891.
15. Schwarz, J.; Böham, V. P. W.; Gardiner, M. G.; Grosche, M.; Herrmann, W. A.; Hieringer, W.; Sieber, G. R. *Chem Eur J* 2000, 6, 1773.
16. Uozumi, Y.; Kimura, T. *Synlett* 2002, 12, 2045.
17. Cai, M. Z.; Huang, Y. Z.; Hu, R. H.; Song, C. S. *J Mol Catal A: Chem* 2004, 212, 151.
18. Cai, M. Z.; Huang, Y. Z.; Hu, R. H.; Song, C. S. *J Mol Catal A: Chem* 2004, 208, 17.
19. Cai, M. Z.; Huang, Y. Z.; Zhao, H.; Song, C. S. *J Organomet Chem* 2003, 682, 20.
20. Xue, L.; Zhou, D. J.; Tang, L.; Ji, X. F.; Huang, M. Y.; Jiang, Y. Y. *React Funct Polym* 2004, 58, 117.
21. Wei, W. L.; Hao, S. J.; Zhou, J.; Huang, M. Y.; Jiang, Y. Y. *Polym Adv Technol* 2004, 15, 287.
22. Vincent, T.; Peirano, F.; Guibal, E. *J Appl Polym Sci* 2004, 94, 1634.
23. Guan, H. M.; Cheng, X. S. *Polym Adv Technol* 2004, 15, 89.
24. Kramareva, N. V.; Stakheev, A. Y.; Tkachenko, O. P.; Klementiev, K. V.; Grünert, W.; Finashina, E. D.; Kustov, L. M. *J Mol Catal A: Chem* 2004, 209, 97.
25. Chang, Y.; Wang, Y. P.; Su, Z. X. *J Appl Polym Sci* 2002, 83, 2188.
26. Wang, H. W.; Sun, W.; Xia, C. G. *J Mol Catal A: Chem* 2003, 206, 199.
27. Sun, W.; Xia, C. G.; Wang, H. W. *N J Chem* 2002, 26, 755.
28. Hardy, J. J. E.; Hubert, S.; Macquarrie, D.; Wilson, A. J. *Green Chem* 2004, 6, 53.
29. Cui, Y. C.; Zhang, L.; Li, Ying. *Polym Adv Technol* 2005, 16, 633.
30. Cai, M. Z.; Song, C. S. *Chem J Chin University* 1998, 19, 1693.
31. Cui, Y. C.; Zhang, L. *J Mol Catal A: Chem* 2005, 237, 120.