

# Polymer-supported Pd(0) catalyst for copper- and ligand-free Sonogashira reactions in aqueous media

Wen-Bin Yi<sup>1,\*</sup>, Xin-Lei Shi<sup>1</sup>, Chun Cai<sup>1</sup>  
and Wei Zhang<sup>2,\*</sup>

<sup>1</sup> School of Chemical Engineering, Nanjing University of Science and Technology, Xiao Ling Wei Street, Nanjing 210094, P.R. China

<sup>2</sup> Department of Chemistry, University of Massachusetts Boston, 100 Morrissey Boulevard, Boston, MA 02125, USA, e-mail: wei2.zhang@umb.edu

\*Corresponding authors

## Abstract

The treatment of commercially available polymethyl methacrylate (PMMA) microspheres with palladium (Pd)Cl<sub>2</sub> and formaldehyde, generated supported Pd(0)-PMMA with 0.79 (wt)% catalyst loading. The catalyst has been used for copper- and ligand-free Sonogashira reactions in aqueous media. It is highly reactive for the reactions of iodobenzenes with aryl acetylenes or alkyl acetylenes. The performance of the recovered catalyst had no significant difference in five cycles. The Pd leaching was detected at a very low level (2.1–9.8 ppm) for each cycle. PMMA-supported PdCl<sub>2</sub>, Pd(OAc)<sub>2</sub>, PdCO<sub>3</sub>, and PdCl<sub>2</sub>(MeCN)<sub>2</sub> have also been tested for Sonogashira reactions.

**Keywords:** aqueous reaction; ligand-free catalysis; polymethyl methacrylate; Sonogashira reaction; supported palladium catalyst.

## 1. Introduction

The Sonogashira cross-coupling of terminal alkynes with aryl halides or vinyl halides is a popular reaction for the generation of sp-sp<sup>2</sup> carbon-carbon bonds [1–4]. A standard Sonogashira reaction requires a palladium (Pd) catalyst, ligand, copper(I) salt co-catalyst and an amine base. The reaction is usually conducted in an aprotic polar solvent such as dimethylformamide (DMF) and dimethylacetamide (DMAC) [5]. This reaction has been widely employed in the synthesis of alkyne-containing aromatic compounds [6, 7], natural products [8–10], medicinal chemistry products [11, 12], oligomers [13, 14], and polymers [15]. However, the following drawbacks associated with Sonogashira reactions have been identified: 1) the copper co-catalyst is sensitive to oxygen, which induces oxidative homocoupling (Glaser-type reaction) of acetylenes to form diacetylenes; 2) copper acetylides are potentially explosive [16]; 3) high boiling point solvents are difficult to remove from the reaction mixture; 4) low reusability of homogeneous Pd catalyst

increases the cost [17]; and 5) the residue contamination of toxic Pd is a major issue in the synthesis of medicinal compounds [18, 19].

Over the years, a significant amount of effort has been directed to the development of modified Sonogashira reactions [17]. Among them, ligand-free Sonogashira reactions reduced the cost and simplified the reaction procedures. Copper-free Sonogashira reactions made the system less sensitive to oxygen and also avoided the formation of the oxidative homocoupling byproduct. Water and other benign solvents have been used to replace high boiling point solvents [20–23]. The development of supported Pd for heterogeneous catalysis is targeted to simplify the catalyst separation process and make the catalyst recyclable. A wide range of materials such as perovskites [24], carbon [25–27], zeolites [28], hydrotalcite [28], silica [29], polyionic gels [30], celluloses [31], and polymers [32] have been used as supports for Pd catalysts. Many of these supported Pd catalysts containing ligands such as triarylphosphines, trialkylphosphines, or *N*-heterocyclic carbenes [32] have been used for reactions in aqueous-organic co-solvent systems containing acetonitrile or DMF [33–36]. In the development of supported Pd catalysts, having an appropriate amount of catalyst loading on the supporting material to ensure catalyst reactivity and reducing catalyst leaching are two major challenges [37, 38]. So far, most of the supported Pd catalysts developed still have ample room for further improvement [39].

From the green chemistry point of view, using supported catalysts for recycling and conducting the reactions in aqueous media is a desirable combination. To our knowledge, ligand-free Pd catalyzed Sonogashira reactions in water have not been well studied [33, 40–43]. Ligand- and copper-free Sonogashira reactions catalyzed by polymer-supported Pd(0) in aqueous media, the topic of this work, have been explored to a lesser extent [44]. Compared to commonly used expensive ligand-containing Pd catalysts such as Pd(PPh<sub>3</sub>)<sub>4</sub>, (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>, and Pd(OAc)<sub>2</sub>/PPh<sub>3</sub>, the polymer-supported Pd(0) catalyst introduced in this paper is more cost effective and has green chemistry advantages. We selected commercially available polymethyl methacrylate (PMMA) microspheres as a polymer support. They are prepared by dispersion polymerization and have a narrow size (0.9–10 μm) distribution [45, 46], which is good for catalyst recycling by filtration. The matrix reinforcement on PMMA is attributed to the existence of an interfacial binding region, which increased the effective filler volume fraction; this enables PMMA to adsorb transition metal hydronium efficiently [47].

We have previously reported the utility of the Pd(0)-PMMA catalyst for the Heck and Suzuki coupling reaction in DMF [48]. The catalyst has good reactivity and recyclability. More importantly, the catalyst has low leaching (<7.8 ppm). Presented in this paper, is our effort to apply Pd(0)-PMMA for ligand- and copper-free Sonogashira reactions in aqueous

media. The performance of the catalyst, including recyclability and metal leaching, has been evaluated.

## 2. Experimental

### 2.1. General information

The  $^1\text{H}$  NMR spectra were recorded on a Bruker Advance RX300 spectrometer (Bruker Corporation, Germany). Gas Chromatography-Mass (GC-MS) analyses were performed on a Saturn 2000GC/MS unit (Varian Corporation, USA). IR spectra were recorded on a Bomen MB154S infrared analyzer (Bomen Corporation, Canada). Field-emission scanning electron microscope (SEM) photographs were recorded on a LEO1530VP unit (LEO Corporation, Germany). Inductively coupled plasma (ICP) spectra were obtained from an Ultima2C apparatus (HORIBA Corporation, France). Microspherical PMMA was obtained from Zongyan Chemical Co. of Suzhou. Palladium catalysts were purchased from Sigma-Aldrich (USA). Commercially available reagents and solvents were used for reactions without further purification. The palladium leaching was measured by ICP analysis of the reaction mixtures. The filtrate of the reaction mixture was diluted with water, extracted with hexane, concentrated to dryness, and then submitted for ICP analysis.

### 2.2. Preparation of Pd-PMMA

PMMA microspheres (15 g) were added to a solution of  $\text{PdCl}_2$  (0.27 g, 1.5 mmol) in 20% HCl, and the mixture was vigorously stirred at  $90^\circ\text{C}$  for 2 h. Formaldehyde (35%, 5 ml) was added and the mixture was stirred at  $90^\circ\text{C}$  for an additional 1 h. After cooling to  $15^\circ\text{C}$ , the pH of the reaction mixture was adjusted to six by the addition of 30% NaOH solution. After stirring at  $15^\circ\text{C}$  for 30 min, the mixture was allowed to stand for about 2 h without stirring. Then, the polymer-supported catalyst was separated by filtration and washed with water (20 ml  $\times$  3) and toluene (20 ml  $\times$  2). The supported catalyst was dried under vacuum at  $120^\circ\text{C}$  for 24 h to give a gray powder (15.13 g). The 0.79 (wt)% Pd loading was determined by ICP analysis.

### 2.3. Typical procedure for Pd-PMMA catalyzed Sonogashira reaction

Iodobenzene (2.04 g, 10 mmol) was added to a mixture of Pd-PMMA (0.67 g, 0.5 mol% Pd) and water (10 ml) in a glass flask under vigorous stirring. After 5 min, phenylacetylene (1.24 g, 12 mmol) and  $\text{Et}_3\text{N}$  (2.2 ml, 15 mmol) were added to the flask. After stirring at  $80^\circ\text{C}$  for 2 h, the mixture was cooled to room temperature and then the catalyst was separated by filtration. The filtrate was diluted with water (10 ml) and extracted with hexane (2  $\times$  10 ml). The combined organic extracts were dried over  $\text{Na}_2\text{SO}_4$  and then *p*-xylene (1.06 g, 10 mmol) was added as an internal standard. A small portion of the solution sample was submitted for GC and GC-MS analyses. The solvents were removed under a vacuum to give

the crude product. A small portion of the solid sample was submitted for ICP analysis to determine the Pd leaching. The crude product was purified by flash column chromatography on silica gel and eluted with cyclohexane to afford diphenylacetylene as a white solid (1.72 g, 94%). The product structure was confirmed by GC-MS and  $^1\text{H}$  NMR analyses.

### 2.4. Typical procedure for catalyst recycling

After conducting the Sonogashira reaction, the mixture was cooled to room temperature and allowed to stand for 30 min without stirring. The catalyst was separated from the reaction mixture by filtration. The solid was washed with water (10 ml  $\times$  3) and toluene (10 ml  $\times$  3). After drying in vacuum at  $120^\circ\text{C}$  for 24 h, the catalyst was ready for the next cycle of the Sonogashira reaction.

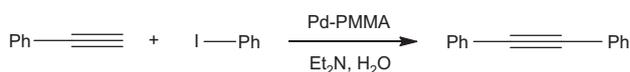
## 3. Results and discussion

### 3.1. Preparation and characterization of Pd-PMMA catalyst

The Pd-PMMA catalyst was prepared following the previously reported procedures [48]. The loading of the Pd-PMMA was determined at 0.79 (wt)% by ICP analysis. A thermal study (TGA) showed that the Pd-PMMA is stable up to  $330^\circ\text{C}$ , which is higher than the blank microspherical PMMA ( $310^\circ\text{C}$ ). Pd-PMMA has good air, moisture, and thermally stabilities.

### 3.2. Pd-PMMA catalyzed Sonogashira reaction of iodobenzene and phenylacetylene

A model Sonogashira reaction was carried out using iodobenzene and phenylacetylene as the substrates (Scheme 1). The Pd-PMMA catalyst was added to a water mixture of



**Scheme 1** Sonogashira reaction of iodobenzene and phenylacetylene in water.

**Table 1** Sonogashira reaction of iodobenzene and phenylacetylene in water.<sup>a</sup>

Entry	[Pd]	Time (h)	Yield (%) <sup>b</sup> of different cycles
1	Pd(0)	2	98 (94), 96, 96, 93, 92
2	$\text{PdCl}_2$	2.5	96 (91), 61, 37
3	$\text{Pd}(\text{OAc})_2$	3	95 (91), 53, 26
4	$\text{PdCO}_3$	4	68 (65)
5	$\text{PdCl}_2(\text{MeCN})_2$	4	59 (57)

<sup>a</sup>Conditions: 10 mmol iodobenzene, 12 mmol phenylacetylene, 0.5 mol% [Pd], 15 mmol  $\text{NEt}_3$ , 10 ml  $\text{H}_2\text{O}$ ,  $80^\circ\text{C}$ .

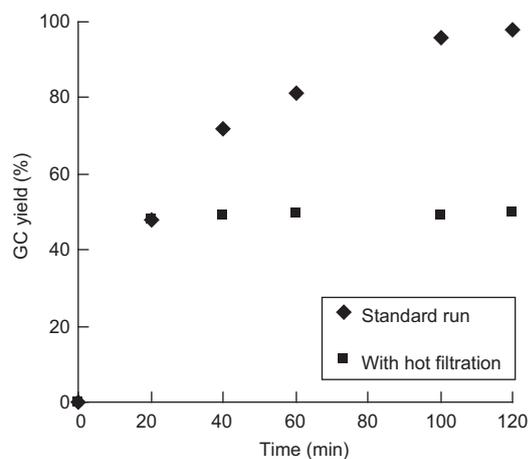
<sup>b</sup>GC yield based on halobenzene. Numbers in parentheses are isolated yields.

iodobenzene and then a slight excess of the acetylene (1.2 equivalent) and  $\text{Et}_3\text{N}$  were added. The reaction mixture was stirred at  $80^\circ\text{C}$ . The coupling product was obtained in 98% GC yield after 2 h (Table 1). Diaryldiacetylene byproducts, which could be generated by the reaction involving the copper(I) co-catalyst, were not detected by GC.

A hot filtration experiment was performed to determine if the Sonogashira reaction is catalyzed by the supported Pd catalyst, or by the leached Pd in solution. The reaction mixture of iodobenzene and phenylacetylene performed at the above-mentioned condition was filtered hot at 20 min to separate the Pd-PMMA from the reaction system. The filtrated solution was returned to the flask and continuously heated at  $80^\circ\text{C}$ . The reaction was monitored by GC and the experimental data was compared with a standard run without the removal of Pd-PMMA (Figure 1). The results show that the reaction was virtually stopped after the removal of Pd-PMMA at 20 min. Its conversion stayed at  $\sim 50\%$ , even after 2 h. On the other hand, the standard reaction, which has no catalyst interruption, afforded quantitative conversion after 2 h.

### 3.3. Pd-PMMA catalyst recycling

The recyclability of Pd-PMMA was evaluated by conducting the Sonogashira reaction of the model reaction of iodobenzene and phenylacetylene. Upon the completion of the reaction following the general procedure described above, the Pd-PMMA was separated by filtration. The washed and dried catalyst was used for the next round of the reaction. The GC yield of diphenylacetylene for five consecutive cycles, was 98%, 96%, 96%, 93%, and 92%, respectively (Table 1, entry 1). No noticeable reduction of activity was observed as indicated by the product yield. This conclusion was supported by the ICP analysis of the reaction mixtures. The Pd leaching was detected at a very low level (2.1–9.8 ppm) for five cycles (Table 2). To have a better understanding of the performance of the recycled catalyst, the GC yield of diphenylacetylene was collected from cycles 1, 3, and 5 at different reaction times. Data sets for cycles 1, 3, and 5 shown in Figure 2



**Figure 1** Removal of catalyst by hot filtration at 20 min versus a standard reaction of iodobenzene and phenylacetylene.

**Table 2** Catalyst leaching and product yield at different cycles.

Cycle	1	2	3	4	5
Pd leaching (ppm)	2.1	3.2	5.0	7.1	9.8
GC yield (%)	100	100	100	100	100

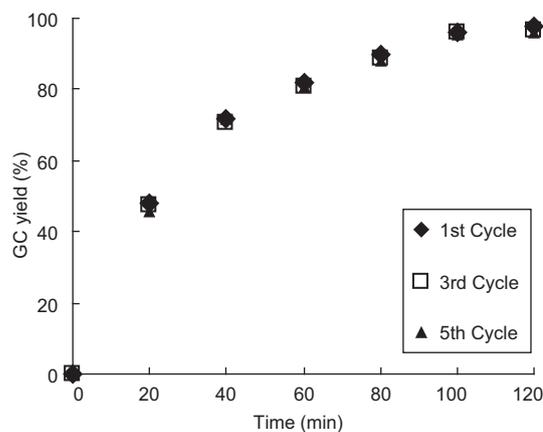
overlapped well. Experiments using the recycled Pd-PMMA catalyst indicated that there was no significant loss of Pd catalyst and no deactivation of catalyst during the recycling process involving filtration, washing, and drying, which confirmed the thermo and chemical stabilities of Pd-PMMA.

### 3.4. Comparison of various PMMA-supported Pd catalysts

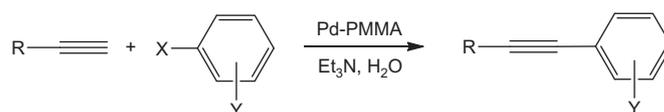
The performances of other PMMA-supported Pd catalysts for the Sonogashira reaction of iodobenzene and phenylacetylene, were also evaluated. It was found that  $\text{PdCl}_2$ -PMMA (Table 1) and  $\text{Pd}(\text{OAc})_2$ -PMMA (Table 1) also have a high reactivity for the reaction conducted at  $80^\circ\text{C}$  for 2.5 h and 3 h, respectively. However, a significant decrease of product yield was observed at the second cycle using the recovered catalysts. A lower product yield may be related to the chemical stability of  $\text{PdCl}_2$  and  $\text{Pd}(\text{OAc})_2$  during the reaction and recycling processes. In the case of using  $\text{PdCO}_3$ -PMMA (Table 1) and  $\text{PdCl}_2(\text{MeCN})_2$ -PMMA (Table 1) as catalysts, both reactions only had moderate conversions and no cycling effort was made for these two catalysts. It is noteworthy that the Sonogashira reaction catalyzed by  $\text{PdCl}_2(\text{PPh}_3)_2/\text{CuI}/\text{Et}_3\text{N}$  or  $\text{Pd}(\text{PPh}_3)_4/\text{CuI}/\text{Et}_3\text{N}$  both gave a trace amount of the desired product.

### 3.5. The scope of the Pd-PMMA catalyzed Sonogashira reactions

To examine the scope of the Pd-PMMA catalyzed Sonogashira reaction, a variety of terminal acetylenes were used to couple



**Figure 2** The Sonogashira reaction of iodobenzene and phenylacetylene at different cycles.

**Table 3** The Sonogashira reactions in the presence of Pd-PMMA in water.<sup>a</sup>

Entry	X	Y	R	Time (h)	Yield (%) <sup>b</sup>
1	I	4-CH <sub>3</sub>	Ph	2	95 (93)
2	I	2-CH <sub>3</sub>	Ph	2	96
3	I	4-OCH <sub>3</sub>	Ph	3	93 (90)
4	I	4-NO <sub>2</sub>	Ph	1	98 (94)
5	I	H	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	4	92
6	I	H	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	4	90 (87)
7	I	H	CH <sub>3</sub> OCO	7	83
8	Br	H	Ph	12	62 (58)
9	Br	4-COCH <sub>3</sub>	Ph	12	85 (82)
10	Br	2-COCH <sub>3</sub>	Ph	12	82
11	Br	4-NO <sub>2</sub>	Ph	12	84
12	Br	4-CF <sub>3</sub>	Ph	12	85
13	Br	3-CF <sub>3</sub>	Ph	12	80
14	Br	3-CHO	Ph	16	85 (81)
15	Br	4-F	Ph	16	81
16	Br	4-CH <sub>3</sub>	Ph	16	50
17	Br	4-OCH <sub>3</sub>	Ph	18	41 (38)
18	Br	2-OCH <sub>3</sub>	Ph	18	43
19	Cl	H	Ph	24	7
20	Cl	H	Ph	32	8 <sup>c</sup>
21	Cl	4-CH <sub>3</sub>	Ph	32	5
22	Cl	4-COCH <sub>3</sub>	Ph	24	13 (11)
23	Cl	2-COCH <sub>3</sub>	Ph	24	11

<sup>a</sup>Conditions: 10 mmol halobenzene, 12 mmol acetylene, 0.5 mol% Pd-PMMA, 15 mmol NEt<sub>3</sub>, 10 ml H<sub>2</sub>O, 80°C.

<sup>b</sup>GC yield based on halobenzene. Numbers in parentheses are isolated yields.

<sup>c</sup>1 mol% of Pd-PMMA was used.

with different phenyl iodides, bromides and chlorides (Table 3). Phenyl iodides containing either electron-donating or electron-withdrawing groups, readily coupled with phenylacetylene (Table 3) and gave excellent product yields. Non aromatic acetylenes, such as 1-heptyne (Table 3) and 1-octyne (Table 3), also afforded products in excellent yields when reacted with phenyl iodide. The reaction of electron-poor alkynes, such as propiolic acid methyl ester with phenylacetylene, gave 83% GC yield (Table 3). The time for the reaction of less reactive bromobenzenes with phenylacetylene was increased to 12–18 h. The reaction of bromobenzenes afforded 62% of diphenylacetylene (Table 3). Electron-poor bromobenzenes containing NO<sub>2</sub>, CF<sub>3</sub>, F or acetyl groups gave coupling products in the range of 81–85% GC yields (Table 3). Electron-rich bromotoluene and bromoanisole were found to be less reactive in giving products in 41–50% GC yields (Table 3). The position of the substitution group on bromobenzenes had no significant influence on product yield. For example, reactions of 4- and 2-bromo acetophenone with phenylacetylene gave coupled products in 85% and 82% GC yield, respectively (Table 3). Much less reactive chlorobenzenes were also tested for the Sonogashira reaction with phenylacetylene. Neither chlorobenzene nor methyl- and acetyl-substituted chlorobenzenes gave good product yields (Table 3) even under the condition of increasing the reaction time to 32 h.

## 4. Conclusions

Pd loaded PMMA microspheres have been introduced as a supported catalyst for the Sonogashira cross-coupling reaction in aqueous media without using ligand and copper(I) salt as a co-catalyst. The recovered catalyst has consistent performance for five cycles with a very low Pd leaching rate (2.1–9.8 ppm). In addition to Heck, Suzuki, and Sonogashira reactions, this highly reactive, chemically stable, and cost effective catalyst could have board applications for other Pd-catalyzed reactions.

## Acknowledgements

WY gratefully acknowledges the financial support of the NUST Excellence Initiative program, NUST Research Funding (2011ZD-JH07), Jiangsu Provincial Natural Science Foundation for Key Projects (BK2010070) and National Natural Science Foundation of China (20902047).

## References

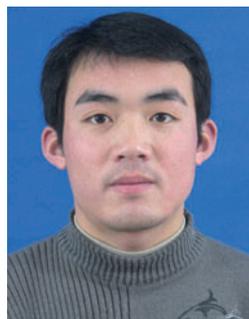
- [1] Sonogashira K, Tohda Y, Hagihara N. *Tetrahedron Lett.* 1975, 16, 4467–4470.

- [2] Sonogashira K, Yatake T, Tohda Y, Takahashi S, Hagihara N. *J. Chem. Soc. Chem. Commun.* 1977, 291–292.
- [3] Takahashi S, Kuroyama Y, Sonogashira K, Hagihara N. *Synthesis* 1980, 627–630.
- [4] Chinchilla R, Nájera C. *Chem. Rev.* 2007, 107, 874–922.
- [5] Sonogashira, K. In *Comprehensive Organic Synthesis*, Trost, BM, Fleming, I, Eds., Pergamon Press: New York, 1991, Vol. 3, pp. 521–561.
- [6] Tykwinski RR. *Angew. Chem. Int. Ed.* 2003, 42, 1566–1568.
- [7] Negishi E, Anastasia L. *Chem. Rev.* 2003, 103, 1979–2017.
- [8] Grissom JM, Gunawardena GU, Klingberg D, Huang D. *Tetrahedron* 1996, 52, 6453–6518.
- [9] Lang P, Magnin G, Mathis G, Burger A, Biellmann JF. *J. Org. Chem.* 2000, 65, 7825–7832.
- [10] Uenishi JI, Matsui K, Ohmiya H. *J. Organomet. Chem.* 2002, 653, 141–149.
- [11] Nicolaou KC, Dai WM. *Angew. Chem. Int. Ed. Engl.* 1991, 30, 1387–1416.
- [12] De Kort M, Correa V, Valentijn ARPM, Van der Marel GA, Potter BVL, Taylor CW, van Boom JH. *J. Med. Chem.* 2000, 43, 3295–3303.
- [13] Ziener U, Godt A. *J. Org. Chem.* 1997, 62, 6137–6143.
- [14] Huang S, Tour JM. *Tetrahedron Lett.* 1999, 40, 3347–3350.
- [15] Francke V, Mangel T, Muellen K. *Macromolecules* 1998, 31, 2447–2453.
- [16] Chinchilla R, Najera C. *Chem. Soc. Rev.* 2011, 40, 5084–5121.
- [17] Molnar A. *Chem. Rev.* 2011, 111, 2251–2320.
- [18] Thayer A. *Chem. Eng. News* 2005, 83, 55–58.
- [19] Garrett CE, Prasad K. *Adv. Synth. Catal.* 2004, 346, 889–900.
- [20] Li CJ. *Chem. Rev.* 2005, 105, 3095–3166.
- [21] Herrerías CI, Yao X, Li Z, Li CJ. *Chem. Rev.* 2007, 107, 2546–2562.
- [22] Doucet H, Hierso JC. *Angew. Chem. Int. Ed.* 2007, 46, 834–871.
- [23] Lubineau A, Auge J. In *Modern Solvents in Organic Synthesis*, Knochel, P, Ed., Springer: Berlin, 1999.
- [24] Lohmann S, Andrews SP, Burke BJ, Smith MD, Atfield JP, Tanaka H, Kaneko K, Ley SV. *Synlett* 2005, 1291–1295.
- [25] Dantas Ramos AL, da Silva Alves P, Aranda DAG, Schmal M. *Appl. Catal. A* 2004, 277, 71–81.
- [26] Batchu VR, Subramanian V, Parasuraman K, Swamy NK, Kumar S. *Tetrahedron* 2005, 61, 9869–9877.
- [27] Raju S, Kumar PR, Mukkanti K, Annamalai P, Pal M. *Bioorg. Med. Chem. Lett.* 2006, 16, 6185–6189.
- [28] Corma A, García H, Primo A. *J. Catal.* 2006, 241, 123–131.
- [29] Crudden CM, Sateesh M, Lewis R. *J. Am. Chem. Soc.* 2005, 127, 10045–10050.
- [30] Thiot C, Schmutz M, Wagner A, Mioskowski C. *Angew. Chem. Int. Ed.* 2006, 45, 2868–2871.
- [31] Reddy KR, Kumar NS, Reddy PS, Sreedhar B, Kantam ML. *J. Mol. Catal. A: Chem.* 2006, 252, 12–16.
- [32] Albéniz AC, Carrera C. *Eur. J. Inorg. Chem.* 2011, 15, 2347–2360.
- [33] Cai MZ, Xu QH, Sha JC. *J. Mol. Catal. A: Chem.* 2007, 272, 293–297.
- [34] Masllorens J, Moreno-Manas M, Pla-Quintana A, Roglans A. *Org. Lett.* 2003, 5, 1559–1561.
- [35] Shimizu K, Koizumi S, Hatamachi T, Yoshida H, Komai S, Kodama T, Kitayama Y. *J. Catal.* 2004, 228, 141–151.
- [36] Cai MZ, Xu QH, Wang PP. *J. Mol. Catal. A: Chem.* 2006, 250, 199–202.
- [37] Leadbeater NE. *Chem. Commun.* 2005, 2881–2902.
- [38] Dijos BML, Vankelecom IFJ, Jacobs PA. *Adv. Synth. Catal.* 2006, 348, 1413–1446.
- [39] Zheng PW, Zhang WQ. *J. Catal.* 2007, 250, 324–330, references cited therein.
- [40] Luo F, Lo H. *J. Organomet. Chem.* 2011, 696, 1262–1265.
- [41] Sawoo S, Srimani D, Dutta P, Lahiri R, Sarkar A. *Tetrahedron* 2009, 65, 4367–4374.
- [42] Liang B, Dai M, Chen J, Yang Z. *J. Org. Chem.* 2005, 70, 391–393.
- [43] Liang B, Dai M, Chen J, Yang Z. *J. Org. Chem.* 2005, 70, 4869–4872.
- [44] Sudeshna S, Dipankar S, Piyali D, Rima L, Amitabha S. *Tetrahedron* 2009, 65, 4367–4374.
- [45] Shen S, Sudol ED, Elaasser MS. *J. Polym. Sci., Part A: Polym. Chem.* 1994, 32, 1087–1100.
- [46] Smigol V, Svec FJ. *Appl. Polym. Sci.* 1992, 46, 1439–1448.
- [47] Cyril A, Denis B, Ralf T, Rolf M. *Chem. Mater.* 2003, 15, 4874–4878.
- [48] Song D, Yi WB. *J. Mol. Catal. A: Chem.* 2008, 280, 20–23.

Received January 23, 2012; accepted February 28, 2012



Dr. Wen-Bin Yi is an Associate Professor in the Department of Pharmaceutical and Fine Chemicals at the Nanjing University of Science & Technology (NJUST). He is currently a Visiting Professor at the University of Massachusetts Boston. He has 60 publications on organometallic catalysis, organocatalysis, fluorine chemistry, and green chemistry.



Xin-Lei Shi received his BS degree in 2006 from Shandong University of Technology. He is currently a graduate student in Prof. Chun Cai's group at NJUST and working on organometallic catalysis.



Dr. Chun Cai is a Professor and the Chairman of the Department of Pharmaceutical and Fine Chemicals at the NJUST. He has published over 100 papers on fluorous biphasic catalysis, fluorine chemistry, organometallic catalysis, and green chemistry.



Dr. Wei Zhang is an Associate Professor and the Director of the Center for Green Chemistry in the Department of Chemistry, University of Massachusetts Boston. He was a Senior Chemist at DuPont Agricultural Products and Director of Discovery Chemistry at Fluorous Technologies, Inc. He has published over 130 papers on free radical chemistry, fluorous chemistry, and green chemistry.