Catalysis Communications 43 (2014) 75–78

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Magnetically recyclable Fe@Pd/C as a highly active catalyst for Suzuki coupling reaction in aqueous solution

Weijie Tang, Jing Li, Xiaodong Jin, Jian Sun, Jingwei Huang, Rong Li *,1

Gansu Provincial Engineering Laboratory for Chemical Catalysis, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

ARTICLE INFO

Article history:
Received 5 July 2013
Received in revised form 29 August 2013
Accepted 2 September 2013
Available online 24 September 2013

Keywords:
Fe@Pd/C catalyst
Core–shell
Suzuki coupling reaction
Aqueous solution
Magnetically recyclable

ABSTRACT

In this work, a novel catalyst Fe@Pd/C was synthesized by sequential reduction method. The core–shell catalyst exhibited efficient catalytic activity in Suzuki coupling reaction at mild condition in water. Moreover, the catalyst could be recycled by external magnetic field and the yields achieved above 86% after reused at least 5 times.

1. Introduction

Platinum-group metals, especially Pd, are excellent and versatile catalysts in various important reactions such as carbon–carbon coupling [1], alcohol oxidation [2], olefin hydrogenation [3] and electrochemical formic acid oxidation [4]. Pd nanoparticles (NPs) have been extensively applied in these reactions due to their high surface-to-volume ratio and ease of synthesis [5,6]. Unfortunately, catalytic reactions usually occur on the surface of a Pd NP catalyst and a large fraction of Pd atoms in the core are inactive [7]. Thus, it becomes a huge challenge that how to take full advantage of Pd atoms and to reduce Pd usage without sacrificing the catalytic performance. At present, the core–shell structure concept has been introduced to solve the difficulty and it has sparked increasing attention for the application of bi-metallic catalysts [8]. In this core–shell structure, the Pd is replaced by other non-noble metals such as Co, Fe, and Ni, which not only greatly reduces their cost but also can remarkably enhance their catalytic activities, as a result of the synergistic structural and electronic effects of the two metals (via the so-called strain and ligand effects) [9–11]. It is well-known that iron is an abundance and magnetism material. When it is successfully employed as the core, the obtained catalysts naturally combine the advantages of low cost and an easy recovery function derived from using of an external magnetic field [12–15].

It is representative that Palladium-catalyzed Suzuki and Heck coupling is a fascinating reaction for the construction of C–C bonds and plays an important role in pharmaceutical industry and organic synthesis [16–19]. Traditionally, the reactions are conducted with homogeneous catalysts, which are effective even with inactivated substrates and provide excellent turnover values [20]. In addition, most of the reaction medium is organic solvent. In this case, some obvious weaknesses appear. The employed organic solvents can be the source of environmental problems. Meanwhile, removing residual palladium and its ligands from the reaction medium is usually a labor-intensive process [21], which restricts the industrial reuse of these catalysts [22–27]. Therefore, we make a try to use heterogeneous catalyst, a kind of excellent catalyst that is usually inexpensive, readily obtained and easily removed from the reaction medium compared with homogeneous catalyst.

On the basis of these observations, we report a simple and efficient method for synthesizing carbon-supported Fe@Pd core–shell catalyst, which can be sufficiently applied for Suzuki reaction in aqueous solution. It could be expected to not only obviously decrease the usage of Pd but also improve yield and reusability compared with commercial Pd/C catalyst.

2. Experiment

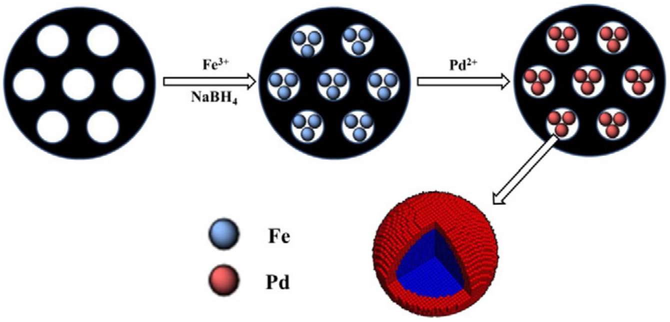
2.1. Characterization methods

Pd content of the catalyst was measured by inductively coupled plasma (ICP) on an IRIS Advantage analyzer. The size and morphology of the magnetic nanoparticles were observed by a Hitachi-600 electron microscope, with an accelerating voltage of 100 kV. XRD measurements were performed on a Rigaku D/max-2400 diffractometer using Cu-K α radiation as the X-ray source in the 2θ range of 10–90°. Magnetic measurements of samples were investigated with a Quantum Design vibrating sample magnetometer (VSM) at room temperature in an applied

---

* Corresponding author.
E-mail address: liyirong@lzu.edu.cn (R. Li).
[1] Tel.: +86 931 891 3597; fax: +86 931 891 2582.

1566-7367/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.catcom.2013.09.001



Scheme 1. The process for the preparation of the Fe@Pd/C catalyst.

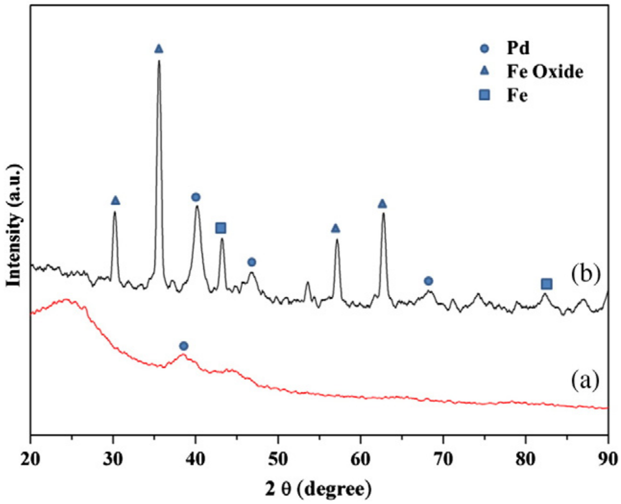


Fig. 2. XRD patterns of (a) commercial 10% Pd/C and (b) Fe@Pd/C.

magnetic field sweeping from −15 to 15 kOe. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI-5702 instrument.

2.2. Catalyst preparation

All chemicals were of analytical grade and used as received without further purification. The carbon supported Fe@Pd core–shell NPs were synthesized by a sequential reduction process [13] as shown in Scheme 1. Firstly, the active carbon (200 mg) was refluxed at 80 °C in nitric acid solution (2 M, 100 mL) for 3 h in order to remove impurities. For preparing Fe@Pd core–shell structured NPs with amorphous Fe core (molar ratio: Pd:Fe = 1:20), 100 mg handled active carbon and 289.6 mg $FeCl_3$ were dispersed in 30 mL water under sonication condition for 20 min. Then excess $NaBH_4$ (676.2 mg) was dissolved in 90 mL water and was added drop-wise into the mixture to reduce Fe^{3+} to Fe^0 (1). The mixture was violently shaken for 30 min till the hydrogen was released completely. Then the Fe/C NPs were collected using a magnet and washed with water and ethanol several times to remove excess sodium borohydride. Then 5 mL $PdCl_2$ solution (0.09 mmol) was added drop-wise in the Fe/C containing water (50 mL) and stirred for 1 h. The atoms in outer-layer of the Fe core were sacrificed to reduce Pd^{2+} to Pd^0 (2). Finally, the products were dried in a vacuum at 50 °C overnight.

$$2FeCl_3 + 6NaBH_4 + 18H_2O \rightarrow 2Fe(s) + 21H_2(gas) + 6B(OH)_3 + 6NaCl \quad (1)$$

$$Fe(s) + Pd^{2+} \rightarrow Fe^{2+} + Pd(s) \quad (2)$$

2.3. Catalytic Suzuki reactions

In a typical procedure, aryl halide (0.5 mmol), phenylboronic acid (0.75 mmol), K_2CO_3 (1.0 mmol), H_2O as solvent (3.0 mL) and the catalyst were taken in a 10 mL round bottom flask. The mixture was stirred for required time and temperature in an air atmosphere. After reaction completion, the catalyst was recovered magnetically by placing a magnet. The products were collected by extraction using ethyl acetate and analyzed by GC (P.E. AutoSystem XL) or GC–MS (Agilent 6890N/5973N). The separated catalyst washed with absolute ethanol could be reused by the addition of new portion substrate after drying at 50 °C under vacuum.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1a shows the transmission electron microscopy (TEM) image of a representative sample. It is seen that the active carbon is of uniform pore shape and the NPs are isolated from each other with relatively homogeneous dispersion on the carbon substrate. Fig. 1b shows the HRTEM image of Fe@Pd/C. In addition, an annular dark-field scanning transmission electron microscopy (STEM) image, together with selected-area element analysis grayscale mapping of C, Fe and Pd (Fig. 1c), shows that Fe (yellow) is distributed on the carbon (red) substrate through the whole area, meanwhile, it reveals a partial covering of Pd atoms (green) on the outer layer of the iron core in the 3D core–shell nanostructures. Due to low content of Pd, the Pd^{2+} is reduced unhomogeneously on Fe core during the process of replacement reaction.

The XRD pattern of the samples Pd/C and Fe@Pd/C is shown in Fig. 2a and b, respectively. The reflection peaks of iron and iron oxide nanocrystals obviously indicate the existence of magnetic components in the

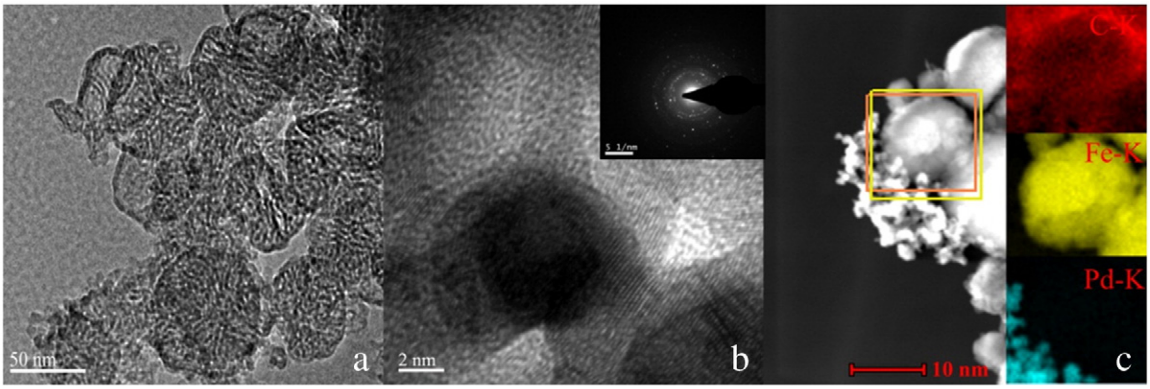


Fig. 1. TEM images of (a) Fe@Pd/C, (b) HR-TEM of Fe@Pd/C and (c) Fe and Pd EDX maps corresponding to the dark-field STEM image.

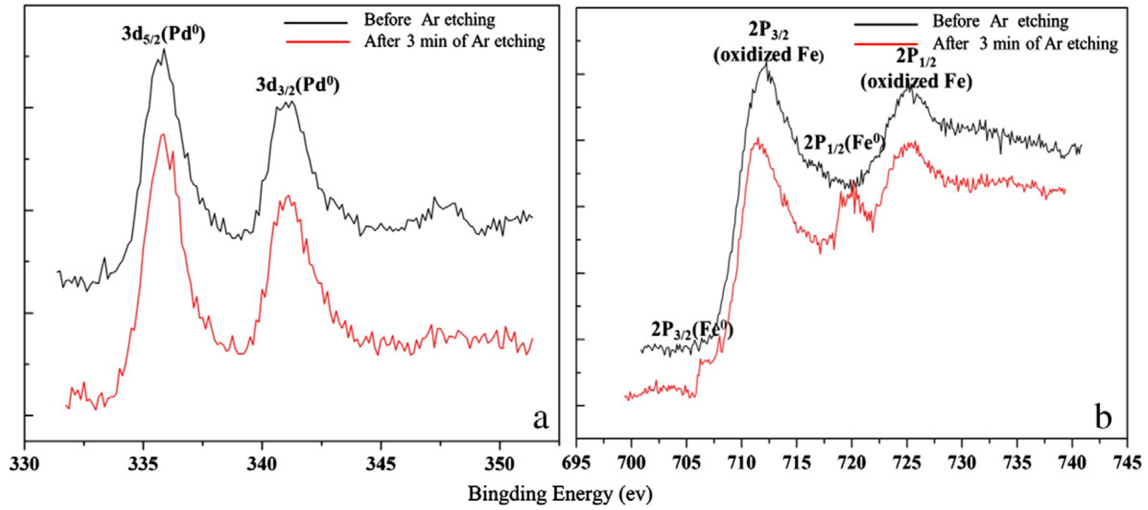


Fig. 3. XPS spectra for Fe@Pd NPs before and after Ar etching. (a) Pd $3d_{5/2}$ and $3d_{3/2}$ peaks, and (b) Fe $2p_{3/2}$ and $2p_{1/2}$ peaks.

as-obtained products. In addition, it is seen that the crystal structure of Pd is face-centered cubic (fcc), diffraction peaks at 2θ values of 40.1°, 46.6°, and 68.0° can be assigned to the (111), (200) and (220) crystal planes, respectively.

XPS spectroscopy, one of the most important techniques to determine the oxidation state of surface elements in materials, was used to characterize the Fe@Pd/C composites. The XPS spectrum of Pd 3d can be fitted into a main doublet peak, as shown in Fig. 3a. The binding energy of the doublet peaks at 335.4 eV (assigned to $Pd^0 3d_{5/2}$) and 340.7 eV (assigned to $Pd^0 3d_{3/2}$) can be attributed to the Pd (0) state. The above results indicate that the Pd species on the surface of the Fe/C nanospheres is elementary Pd (0) and no PdO existed in the Fe@Pd/C composites. Additionally, two types of Fe species are detected (Fig. 3b): Fe^0 (Fe $2p_{3/2}$ located at 706.75 eV) and oxidized Fe (Fe $2p_{3/2}$ located at 710.7 eV). These oxidized Fe species are those from the outer layer of the iron core. In order to probe the core–shell structure of the particles, we conducted the Ar sputtering experiments. The results show that the molar ratio of Fe/Pd increases after Ar sputtering, which indicates that more Pd atoms were etched than Fe atoms. This result is in accordance with a core–shell structure including a core mainly made of Fe and a shell mainly made of Pd.

Fig. 4 shows the magnetization curves of the Fe@Pd/C. It can be seen that the saturation magnetization of the obtained catalyst is 14 emu/g, which represents its excellent magnetism. Thus, our catalyst can be recovered by external magnetic field.

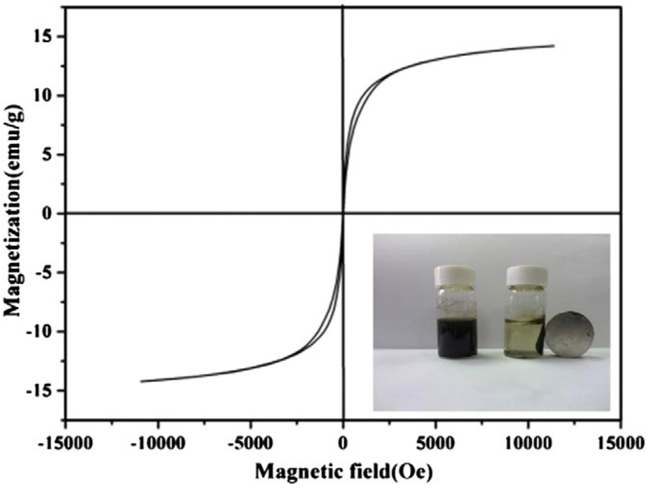


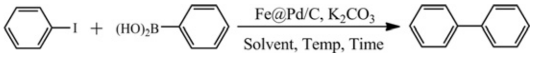
Fig. 4. Room temperature magnetization curve of Fe@Pd/C.

3.2. Catalytic Suzuki reaction

In this study, we firstly tested the performance of Fe@Pd/C catalyst in the Suzuki reaction of iodobenzene with phenylboronic acid in different solvents (ethanol and water) as a model reaction. As shown in Table 1, the coupling reaction in the presence of 1.0 mol% catalyst and K_2CO_3 as a base at 50 °C for 0.5 h in ethanol afforded the corresponding product in excellent yield (entry 1). When the loading of catalyst was decreased to 0.5 mol% and raised the temperature to 60 °C, the yield was almost unchanged (entry 2–3). Upon changing the temperature and time, the reactions were coupled well with only 0.5 mol% of catalyst at 70 °C for 0.5 h in aqueous solution (entries 4–7). The best catalytic activity of the catalyst was found in H_2O solvent together with K_2CO_3 for required time, the optimized condition was thus used for all further studies.

Further, we investigated the general applicability of Fe@Pd/C in the coupling of various aryl halides under the optimized condition. As shown in Table 2, the coupling of aryl iodide derivatives proceeded smoothly at 70 °C for 0.5 h and the corresponding products obtained high yields (entries 1–5). Then we explored the catalytic activity for the coupling of aryl bromides and lengthened reaction time to 1 h. In this condition, aryl bromides and their derivatives efficiently reacted with phenylboronic acids and obtained excellent yields (entries 6–11). It was interesting to note that aryl iodides and bromides with electron-donating groups such as $-CH_3$, $-OCH_3$ and $-OH$ bring good yields (entries 2, 4–5, 7, 9), however, aryl iodides and bromides with electron-withdrawing group obtained excellent yields (entries 3, 8, 10). Besides, the protocol tolerated the presence of functional groups in the -ortho and -meta positions of the aryl halides (entries 5, 9–10). Then, in order to test the feasibility of this protocol for challenging substrates, we

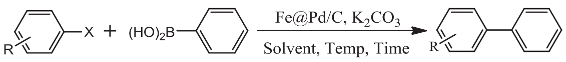
Table 1
The Suzuki reaction of iodobenzene with phenylboronic acid using Fe@Pd/C catalyst.[a]

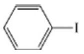
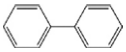
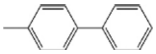
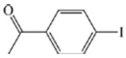
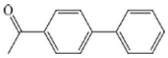
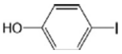
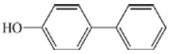
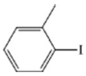
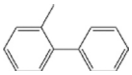
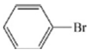
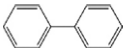
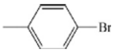
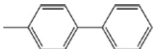
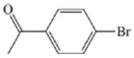
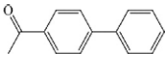
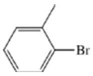
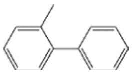
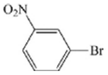
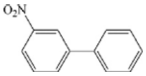
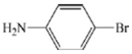
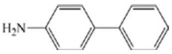
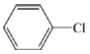
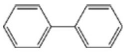
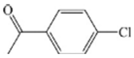
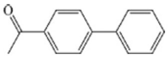


Entry	Solvent	Catalyst (mol%)	Temp (°C)	Time (h)	Yield (%)[b]
1	EtOH	1.0	50	0.5	100
2		0.5	50	0.5	99
3		0.5	60	0.5	100
4	H_2O	0.5	50	1.0	71
5		0.5	60	1.0	78
6		0.5	70	1.0	100
7		0.5	70	0.5	100

[a] Reaction condition: iodobenzene (0.5 mmol), phenylboronic (0.75 mmol), K_2CO_3 (1.0 mmol), solvent (3.0 mL), Pd catalyst (0.5–1.0 mol%), and 50–70 °C.
[b] Yield was determined by GC analysis.

Table 2
The Suzuki reaction of aryl halides with phenylboronic acid using Fe@Pd/C catalyst.[a]



Entry	Aryl halide	Product	Temp (°C)	Time (h)	Yield (%)[b]
1			70	0.5	100 (51[d])
2			70	0.5	92 (45[d])
3			70	0.5	98 (43[d])
4			70	0.5	94
5			70	0.5	97
6			80	0.5	97 (30[d])
7			80	1	91 (22[d])
8			80	1	90 (27[d])
9			80	1	95
10			80	1	93
11			80	1	85
12			100	6	20[c]
13			130	6	34[c]

[a] Reaction condition: aryl halide (0.5 mmol), phenylboronic (0.75 mmol), K_2CO_3 (1.0 mmol), H_2O (3.0 mL), Pd catalyst (0.5 mol%), 70–130 °C.

[b] Yield was determined by GC analysis.

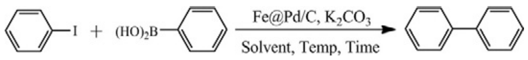
[c] The loading of Pd catalyst is 1.0% mol.

[d] Aryl halide (0.5 mmol), phenylboronic (0.75 mmol), K_2CO_3 (1.0 mmol), H_2O (3.0 mL), 10% Pd/C catalyst (Pd: 0.5 mol%), 70–80 °C.

conducted the coupling of several aryl chlorides with phenylboronic acid, however, poor yields were obtained in the reactions with 1.0 mol% under 100–130 °C for 6 h (entries 12–13). Furthermore, we studied the activity of commercial Pd/C (10%) catalyst using some substrate (entries 1–3, 6–8), and the catalyst exhibited far less active for Suzuki coupling reaction than the Fe@Pd/C catalyst.

The recyclability of Fe@Pd/C was further investigated because the recyclability of the heterogeneous catalyst was one of the most important issues for practical applications. After the separation from reaction mixture by magnet, the catalyst had been reused in model reaction for five reaction cycles. As shown in Table 3, the yields were above 86% in all five reaction cycles and the decreased catalytic activity as recycling proceeded might be due to the significant loss of palladium. Metal leaching of the catalyst before and after reaction was studied by ICP-AES analysis. The Pd content was found to be 2.95 wt.% before reaction and 2.71 wt.% after five reaction cycles, which is not a negligible amount of metal loss actually. How to avoid or reduce as far as possible the metal loss in catalytic reaction has always been the focus of our study.

Table 3
Reuse of Fe@Pd/C catalyst in Suzuki reaction of iodobenzene with phenylboronic acid.



Recycle time	1	2	3	4	5
Yield (%)	100 (2.95[a])	95 (2.88[a])	91 (2.83[a])	90 (2.79[a])	86 (2.71[a])

[a] The changes of Pd content during five reaction cycles.

4. Conclusions

In summary, we demonstrate a simple approach for synthesizing Fe@Pd/C catalyst by a two step process. The resultant catalyst combines many advantages such as low cost, long-term stability, high catalytic activity and easy recovery for Suzuki coupling reaction in water. Furthermore, it can be used repeatedly 5 times with minor variation of catalytic activity. Various characterization methods are presented, which proves that the Fe@Pd/C catalyst is very promising for the application in Suzuki C–C coupling reaction.

Acknowledgment

This work was supported by the Gansu Provincial Engineering Laboratory for Chemical Catalysis, and the Projects in Gansu Province Science and Technology Pillar Program (1204GKCA047).

References

[1] T.E. Barder, S.D. Walker, J.R. Martinelli, S.L. Buchwald, J. Am. Chem. Soc. 127 (2005) 4685–4696.
[2] N. Kakiuchi, Y. Maeda, T. Nishimura, S. Uemura, J. Org. Chem. 66 (2001) 6620–6625.
[3] Y.Q. Wang, S.M. Lu, Y.G. Zhou, J. Org. Chem. 72 (2007) 3729–3734.
[4] V. Mazumder, S.H. Sun, J. Am. Chem. Soc. 131 (2009) 4588–4589.
[5] M.T. Reetz, E. Westermann, Angew. Chem. Int. Ed. 39 (2000) 165–168.
[6] V. Kogan, Z. Aizenshtat, R. Popovitz-Biro, R. Neumann, Org. Lett. 4 (2002) 3529–3532.
[7] J.D. Aiken, R.G. Finke, J. Mol. Catal. A Chem. 145 (1999) 1–44.
[8] R.G. Chaudhuri, S. Paria, Chem. Rev. 112 (2012) 2373–2433.
[9] N. Kristian, Y.L. Yu, J.M. Lee, X.W. Liu, X. Wang, Electrochim. Acta 56 (2010) 1000–1007.
[10] H.L. Jiang, Q. Xu, J. Mater. Chem. 21 (2011) 13705–13725.
[11] P. Mani, R. Srivastava, P. Strasser, J. Phys. Chem. C 112 (2008) 2770–2778.
[12] D.L. Huber, Small 1 (2005) 482–501.
[13] X.B. Zhang, J.M. Yan, S. Han, H. Shioyama, Q. Xu, J. Am. Chem. Soc. 131 (2009) 2778–2779.
[14] D. Kim, J. Park, K. An, N.K. Yang, J.G. Park, T. Hyeon, J. Am. Chem. Soc. 129 (2007) 5812–5813.
[15] A.H. Lu, E.L. Salabas, F. Schuth, Angew. Chem. Int. Ed. 46 (2007) 1222–1244.
[16] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457–2483.
[17] P. Lloyd-Williams, E. Giralt, Chem. Soc. Rev. 30 (2001) 145–157.
[18] J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 102 (2002) 1359–1469.
[19] A. Fihri, M. Bouhrara, B. Nekoueishahraki, J.M. Basset, V. Polshettiwar, Chem. Soc. Rev. 40 (2011) 5181–5203.
[20] R.B. Bedford, S.L. Hazelwood, M.E. Limmert, Chem. Commun. 22 (2002) 2610–2611.
[21] C.E. Garrett, K. Prasad, Adv. Synth. Catal. 346 (2004) 889–900.
[22] C. Baleizao, A. Corma, H. Garcia, A. Leyva, J. Org. Chem. 69 (2004) 439–446.
[23] M. Mora, C. Jimenez-Sanchidrian, J.R. Ruiz, J. Mol. Catal. A Chem. 285 (2008) 79–83.
[24] C. Liu, Y.X. Zhang, N. Liu, J.S. Qiu, Green Chem. 14 (2012) 2999–3003.
[25] A.N. Marziale, S.H. Faul, T. Reiner, S. Schneider, J. Eppinger, Green Chem. 12 (2010) 35–38.
[26] S. Li, W. Zhang, M.-H. So, C.-M. Che, R. Wang, R. Chen, J. Mol. Catal. A Chem. 359 (2012) 81–87.
[27] W. Zhang, Q. Wang, F. Qin, H.M. Zhou, Z. Lu, R. Chen, J. Nanosci. Nanotechnol. 11 (2011) 7794–7801.