DOI: 10.1002/cctc.201200129

Preparation of Recoverable Pd Catalysts for Carbonylative Cross-Coupling and Hydrogenation Reactions

Jian-Rui Niu, Xing Huo, Feng-Wei Zhang, Hai-Bo Wang, Ping Zhao, Wu-Quan Hu, Jiantai Ma,* and Rong Li*[a]

We report on the synthesis, characterization and catalytic performance of new, supported Pd^{II} and Pd^0 catalysts. The catalysts are characterized by TEM, XRD, FTIR, X-ray photoelectron spectroscopy, and vibrating sample magnetometry. The catalysts are found to be active in both forms, Pd^{II} and Pd^0, for the carbonylative cross-coupling reaction of aryl iodides with arylboronic acids, and for the hydrogenation of aromatic nitro- and unsaturated compounds. The newly developed catalysts are prepared by a synthetic strategy that is similar to the one used for other supported catalysts but are easier to recover—they can be recycled by magnetic separation from liquid phase reactions—and can be used for at least 5 consecutive trials without any decrease in activity.

Introduction

Biaryl ketones are important moieties in many biologically active molecules, natural products, and pharmaceuticals. A variety of methods for their preparation have been reported.[1] The Suzuki carbonylative coupling reaction is one of the most promising methods for the direct synthesis of biaryl ketones from carbon monoxide, aryl halides, and arylboronic acids, owing to the wide variety of functionalities that can be tolerated on either partner and the fact that arylboronic acids are generally nontoxic and thermally-, air-, and moisture-stable.[2] As a result of improvements in selectivity and activity, the interest in homogeneous catalysts has grown dramatically. Nevertheless, one key challenge for the commercial development and practical use of homogeneous catalysts is the separation of product from the catalytic media. This process is often complicated and usually accomplished by means of complex work-up procedures.[3] Attempts to improve catalyst recovery and recycling, include the use of biphasic systems[4] or the immobilization of catalysts on solids.[5] In such circumstances, systems that use silica-coated magnetic nanoparticles (MNPs) have drawn attention. These systems, which are comprised of magnetically recoverable solid supports, can be easily and quickly removed from the reaction medium, and are used in fields such as drug delivery,[6] magnetic resonance imaging,[7] biomolecular sensors,[8] bioseparations,[9] and magneto-thermal therapy.[10] In this study, Pd complexes were immobilized on this type of support to create heterogeneous catalysts because they are easily handled, recyclable, and the process is “green”.[11] To enhance the stability, we used coated (MNPs) for the metal immobilization.

A number of functionalized MNPs have been employed in a range of organic transformations, and show excellent catalytic activities in C–C coupling,[12] hydrogenation,[13] oxidation,[14] amination,[15] and nitrile hydration reactions.[16] Inspired by the work of Fryxell et al.[17] and Pinnavaia and Mercier,[18] who demonstrated that thiol-modified mesoporous materials are remarkable scavengers for mercury, and by Kang et al.,[19–20] who showed that SBA-15-SH has a higher affinity for Pd and Pt compared with other metals, we began a study into the immobilization of Pd on a mercaptopropyl-modified silica-coated magnetic support with great catalytic and separation properties. We hoped that the functionalized magnetic catalyst would act as both a support, and as a scavenger for any small amounts of residual Pd that escaped from the surface.[21] The supported Pd^{II} catalyst is active towards selective conversion in the carbonylative Suzuki coupling reaction and the minimization of waste generation, which is highly relevant to the development of “green” chemical processes. If the metal is properly reduced, Pd^0 nanoparticles immobilized on the magnetic support surface are obtained, and the catalyst becomes active for hydrogenation reactions. We present here a reusable Pd catalyst supported on a magnetic material for carbonylative cross-coupling and hydrogenation reactions.[22]

Results and Discussion

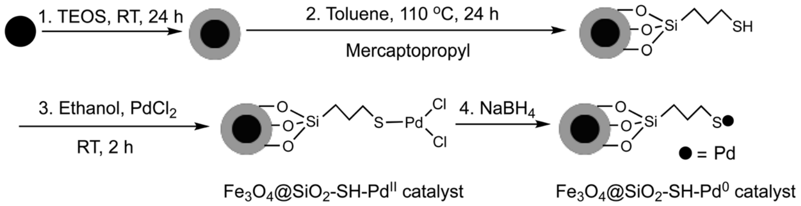
Catalyst preparation and characterization

The preparation of the Fe_3O_4@SiO_2-SH-Pd^{II} catalyst follows the steps described in Scheme 1. Firstly, the silica-coated MNPs

---

[a] J.-R. Niu, X. Huo, F.-W. Zhang, H.-B. Wang, P. Zhao, W.-Q. Hu, Prof. J. Ma, Prof. R. Li
Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization
College of Chemistry and Chemical Engineering
Lanzhou University
222 Tianshui South Road, Lanzhou 730000 (P.R. China)
Fax: (+86) 0931-891-2582 (J.M.)
(+86) 0931-891-2311 (R.L.)
E-mail: majiantai@lzu.edu.cn
liyirong@lzu.edu.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201200219.



Scheme 1. Preparation of the catalysts.

were prepared by a reverse microemulsion. Then, the silica-coated MNPs were functionalized with mercaptopropyl trimethoxysilane. Finally, under reflux conditions, PdCl$_2$ was supported on the surface of ligand-modified MNPs.

The typical TEM image of Fe$_3$O$_4$@SiO$_2$-SH nanoparticles prepared by a reverse microemulsion procedure is shown in Figure 1 a. As can be seen from the image, the average diameter of the as-synthesized spherical particles was about 35 nm and nearly monodisperse. The Fe$_3$O$_4$@SiO$_2$-SH-Pd^0 catalyst didn't change considerably after attachment of the Pd onto the surface of the MNPs (Figure 1 c). It can also be concluded that the Pd particle size distribution was centered at 5 nm, which, unfortunately, indicates that agglomeration occurred (Figure 1 c).

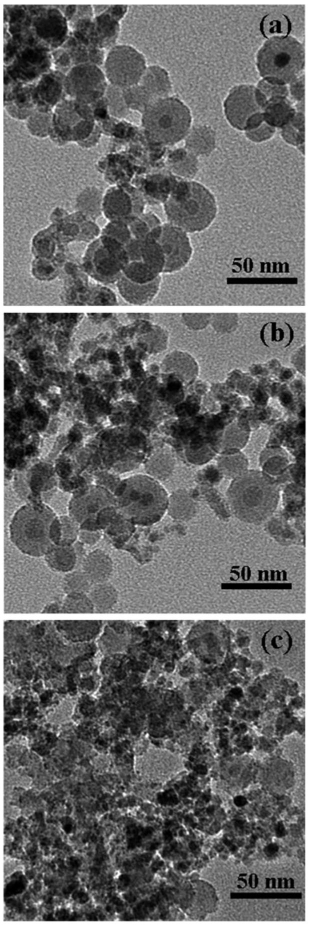


Figure 1. TEM images of (a) Fe$_3$O$_4$@SiO$_2$-SH, (b) Fe$_3$O$_4$@SiO$_2$-SH-Pd^{II}, and (c) Fe$_3$O$_4$@SiO$_2$-SH-Pd^0.

Unambiguous evidence of Pd particles on Fe$_3$O$_4$@SiO$_2$-SH is provided by XRD. The XRD pattern of Fe$_3$O$_4$@SiO$_2$ shows characteristic peaks of magnetite nanoparticles and the sharp, strong peaks confirm the products are well-crystallized. The XRD results reveal their high crystallinity, which is in agreement with the results reported by Li et al.[23] As shown in Figure 2 b and c, the new peaks that appeared are attributed to the Pd species. The results from XRD imply that the Pd nanoparticles have been successfully immobilized on the surface of MNPs.

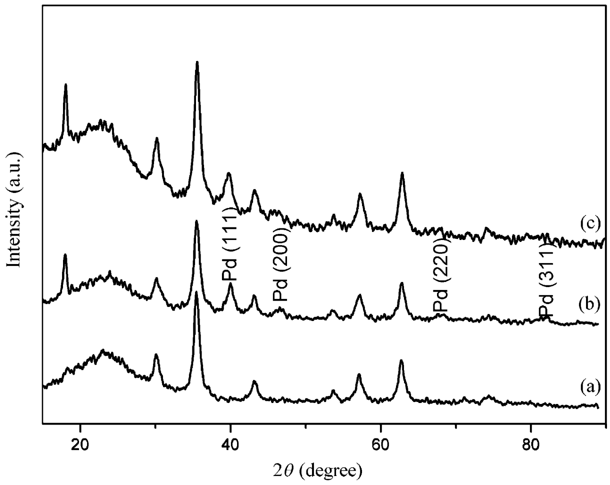


Figure 2. XRD patterns of (a) Fe$_3$O$_4$@SiO$_2$-SH, (b) Fe$_3$O$_4$@SiO$_2$-SH-Pd^{II}, and (c) Fe$_3$O$_4$@SiO$_2$-SH-Pd^0.

The XPS elemental survey scans of the surface of the solid catalyst are shown in Figure 3. The peaks corresponding to C,

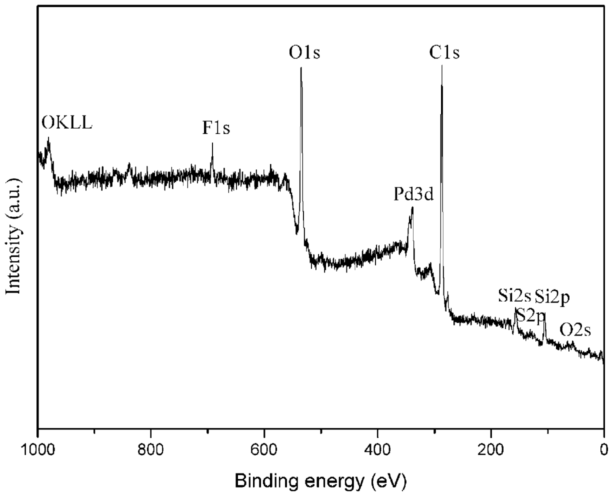


Figure 3. XPS spectrum of the elemental survey scan of Fe$_3$O$_4$@SiO$_2$-SH-Pd^{II}.

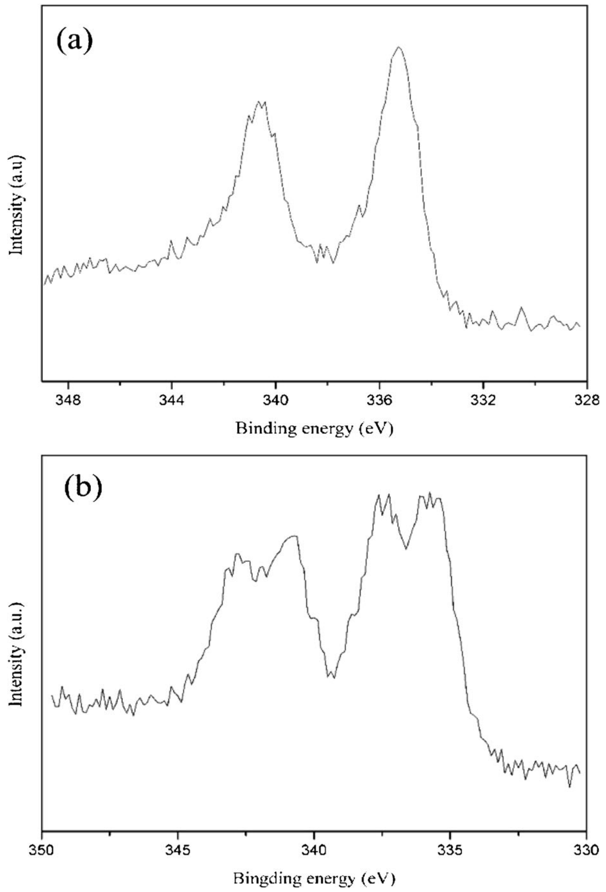


Figure 4. XPS spectrum of (a) $Fe_3O_4@SiO_2$-SH-Pd^0 and (b) $Fe_3O_4@SiO_2$-SH-Pd^{II}, which shows the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies.

Cl, O, Pd, S, and Si are clearly observed. The Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies of $Fe_3O_4@SiO_2$-SH-Pd^{II} were determined to be 343.8 and 338.4 eV, respectively (Figure 4). These values agree with the Pd^{II} binding energy of the complex. Unfortunately, the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ binding energies changed to 336 and 341 eV, which corresponds to the Pd^0 binding energy. The XPS results showed that Pd^0 was formed during the catalyst preparation. This is probably attributable to a small amount of Pd^{II} ions that were reduced by the mercaptopropyl group.

Magnetic measurements were performed by using a vibrating sample magnetometer at room temperature. The magnetization curves for $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2$-SH, and $Fe_3O_4@SiO_2$-SH-Pd^{II} are compared in Figure 5. There was no hysteresis in the magnetization for the three types of nanoparticles. Neither coercivity nor remanence was observed, which suggests that the three nanoparticles are superparamagnetic. The observed saturation magnetizations were 13.83 emu g^{-1} for $Fe_3O_4@SiO_2$, 11.7 emu g^{-1}, 14.5 for $Fe_3O_4@SiO_2$-SH, and 10.6 emu g^{-1} for $Fe_3O_4@SiO_2$-SH-Pd^{II}.The decrease in saturation magnetization might be responsible for the increased mass of mercaptopropyl on the surface of the MNPs. However, the nanomaterials still retained good magnetic properties and could be completely and quickly separated from the aqueous solution by placing a magnet near the reaction vessels.

Catalyst testing for the hydrogenation reaction

The hydrogenation results of aromatic nitro- and unsaturated compounds with different substituent groups as catalyzed by $Fe_3O_4@SiO_2$-SH-Pd are shown in Table 1. The hydrogenation reactions were performed in ethanol, at room temperature and under a 1 atm pressure of H_2. The catalyst was found to be effective for the hydrogenations of these compounds under mild conditions. As shown in Table 1, the hydrogenation reactions reached completion within 50 min, except for 1-nitronaphthalene and trans-stilbene, which required 90 min. Further experiments with the substrate nitrobenzene were performed to verify the catalyst recyclability. After each hydrogenation reaction, the catalyst was easily separable by the application of a magnetic field, the product could be removed with a syringe, and new portions of the substrate were added to the reactor. The new Pd magnetically-separable catalyst could be reused for up to eight successive hydrogenation reactions without a change in substrate conversion after 50 min (100% conversion). In contrast, commercial 10% Pd/C was used to catalyze the hydrogenation of nitrobenzene, and the reaction took 2 h to reach completion, whereas the reaction with $Fe_3O_4@SiO_2$-SH-Pd required no more than 1 h with a relatively low Pd loading under similar experimental conditions.

Owing to the use of the magnetic property, the time interval for both the catalyst separation and product removal is insignificant compared with the time consumed during the reaction. Such a procedure also avoids unnecessary use of other separation techniques such as filtration, decantation, and centrifugation, which greatly simplifies the workup procedure Moreover, the Pd content (3.81 wt%) of the recovered $Fe_3O_4@SiO_2$-SH-Pd catalyst remained approximately the same as that of the fresh catalyst, which indicates that Pd leaching was negligible.

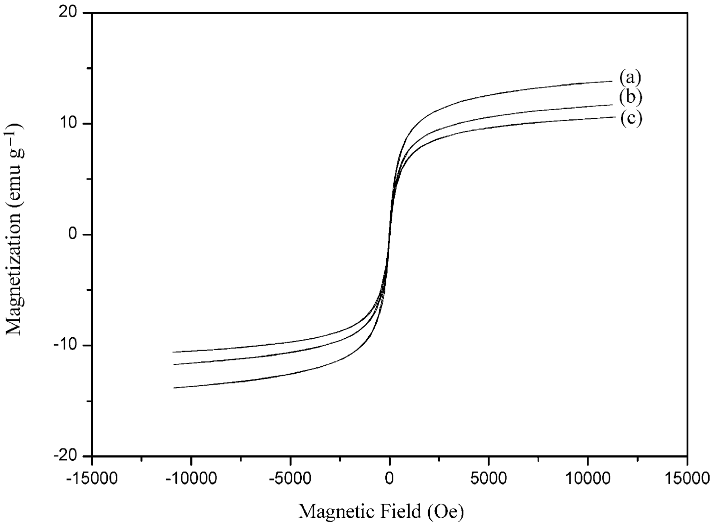
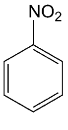
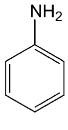
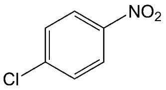
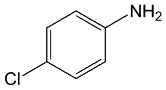
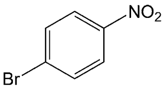
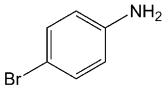
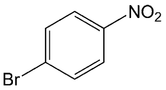
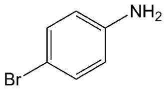
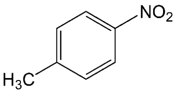
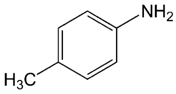
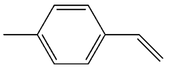
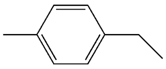
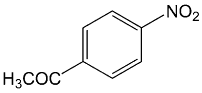
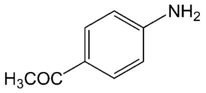
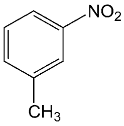
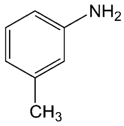
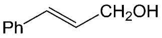
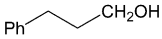
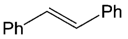
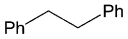
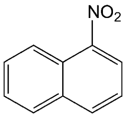
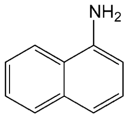


Figure 5. The magnetization curves of (a) $Fe_3O_4@SiO_2$, (b) $Fe_3O_4@SiO_2$-SH, and (c) $Fe_3O_4@SiO_2$-SH-Pd^{II}.

Table 1. Hydrogenation of various substrates by Fe_3O_4@SiO_2-SH-Pd^0.[a]

Entry	Substrate	Product	Reaction time [min]	Yield [%]
1			50	>99
			50	>99[b]
			120	>99[c]
2			50	100
3			50	96
4			45	92[d]
5			50	97
6			50	>99
7			50	97
8			50	98
9			50	99
10			90	99
11			90	92

[a] Reaction conditions: 20 mg catalyst, H_2 atmosphere ($p = 1$ atm), 1 mmol substrate in 5 mL ethanol. [b] Yield after 5 runs. [c] Hydrogenation with 10% Pd/C. [d] Hydrogenation with 20 mg 8.43% Fe_3O_4-NH_2-Pd.

Carbonylative Suzuki coupling reaction

The activity of Pd complexes immobilized on Fe_3O_4@SiO_2 was tested in the Suzuki carbonylative coupling reactions of aryl halides, namely the reactivity of aryl halides with arylboronic acids with K_2CO_3 as a base under balloon pressure of CO in anisole. Firstly, the Suzuki carbonylative reaction of iodobenzene with phenylboronic acid was chosen as the model reaction to evaluate the reaction time. The catalyst was active with nearly 92% conversion in 8 h, and the products of the diphenyl ketone were highly selective (Table 2, entries 1–3). Further investigation of the substrate scope was performed under optimized reaction conditions. As shown in Table 2, various aryl iodides and arylboronic acids were examined and good functional group tolerance of the Fe_3O_4@SiO_2-SH-Pd^{II} catalytic system was observed. For example, aryl iodides containing electron-withdrawing groups, including 4-CH_3CO and 2-NO_2, produced desired ketones in excellent yields (entries 15–20). Notably, up to a 99.7% yield of unsymmetrical biaryl ketone was obtained for 4-chlorobenzeneboronic acid with 4-iodonitrobenzene (Table 2, entry 17). In addition, both 4-methylbenzeneboronic acid and 4-chlorophenylboronic acid reacted smoothly with aryl iodides to give unsymmetrical biaryl ketones in high yields (Table 2, entries 4, 5, 7, 8, 10, 11, 13, 14, 16, 17, 19, and 20).

Recyclability of Fe_3O_4@SiO_2-SH-Pd^{II}

After the first cycle of the reaction, the catalyst was recovered with the help of a magnet, successively washed with distilled water (to remove an excess of base) and ethanol, and then dried at room temperature ready for the next cycle. The carbonylative cross-coupling reactions of 4-iodoacetophenone with phenylboronic acid catalyzed by recycled catalyst are displayed in Table 3.

The hydrogenation reaction of 4-bromonitrobenzene was also catalyzed by Fe_3O_4-SH-Pd and Fe_3O_4-NH_2-Pd (Table 4). Again, the catalyst showed good activity, and Pd leaching was not detected (entry 1). Interestingly, although the amine-functionalized catalyst was also active, Pd leaching was substantial, 0.017% (entry 2), which illustrated the importance of the thiol-modified surface for retaining Pd, which was determined by inductively coupled plasma mass spectrometry.

Conclusions

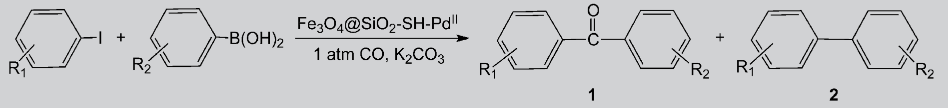
We have developed a novel, practical and economic heterogeneous catalytic system for the Suzuki carbonylative cross-coupling reaction by using mercaptopropyl-modified MNPs that are supported on Pd as the catalyst in anisole under an atmospheric pressure of carbon monoxide. This novel Pd catalyst can be conveniently prepared by the general method, it exhibits higher activity and selectivity for the Suzuki carbonylative coupling reaction and hydrogenation reactions and could be reused five times without significant loss in catalytic activity and selectivity. Our catalyst also avoids the use of phosphine ligands, which renders it more environmentally friendly.

Experimental Section

Synthesis of the hydrophobic magnetite nanoparticles (Fe_3O_4 NPs)

The Fe_3O_4 NPs were prepared by using a published method with a slight modification.[24] Firstly, $FeCl_3\cdot 6H_2O$ (4.8 g), $FeCl_2\cdot 4H_2O$ (2.0 g), and oleic acid (1.0 mL)were added to deionized water (40 mL) under vigorous stirring. Secondly, the mixture solution was purged with nitrogen gas for 30 min. The mixture solution was then heated to 90 °C. Finally, ammonium hydroxide (10 mL, 28 wt%) was added rapidly to the solution, and it immediately turned black. The reaction was kept at 90 °C for 2.5 h. The black precipitate was obtained with the help of a magnet and resuspended in cyclohexane for further processing.

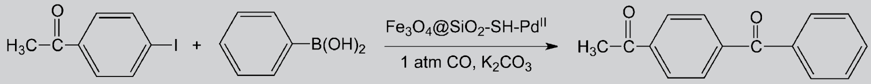
Table 2. Suzuki carbonylative coupling reaction of various aryl iodides with arylboronic acids in the presence of the $Fe_3O_4@SiO_2$-SH-Pd^{II} catalyst.[a]



Entry	R_1	R_2	Reaction time [h]	Yield[b] [%] 1	2
1	H	H	4	72	28
2	H	H	6	87	13
3	H	H	8	91	9
4	H	4-CH_3	8	81	19
5	H	4-Cl	8	85	15
6	4-CH_3	H	8	93	6
7	4-CH_3	4-CH_3	8	91	7
8	4-CH_3	4-Cl	8	93	7
9	4-CH_3O	H	8	92	8
10	4-CH_3O	4-CH_3	8	94	5
11	4-CH_3O	4-Cl	8	99	0.3
12	2-NH_2	H	12	89	11
13	2-NH_2	4-CH_3	12	88	11
14	2-NH_2	4-Cl	12	92	7
15	2-NO_2	H	6	97	0.4
16	2-NO_2	4-CH_3	6	97	2
17	2-NO_2	4-Cl	6	99	<0.1
18	4-CH_3CO	H	6	91	9
19	4-CH_3CO	4-CH_3	6	96	2
20	4-CH_3CO	4-Cl	6	86	13

[a] The reactions were performed with aryl iodide (0.5 mmol), arylboronic acid (0.6 mmol), CO (1 atm), K_2CO_3 (1.5 mmol), and Pd catalyst (1 mol%) in anisole (5 mL) at 80 °C. [b] Determined by GC.

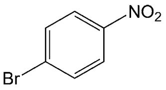
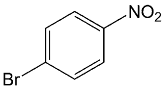
Table 3. The carbonylative cross-coupling reaction of 4-iodoacetophenone with phenylboronic acid catalyzed by recycled catalyst.[a]



Recycle	Catalyst cycle	Yield [%]
1	1	91
5	5	89

[a] The reactions were performed with 4-iodoacetophenone (0.5 mmol), $PhB(OH)_2$ (0.6 mmol), CO (1 atm), K_2CO_3 (1.5 mmol), and Pd catalyst (1 mol%) in anisole (5 mL) at 80 °C.

Table 4. Fe_3O_4-modified-Pd catalysts for the hydrogenation reaction.

Entry	Substrate	Catalyst (loading)	Reaction time [min]	Yield [%]	Pd leaching [%]
1		Fe_3O_4-SH-Pd reused 5 times (3.81 %)	50	96	n.d.
2		Fe_3O_4-NH_2-Pd reused 5 times (8.43 %)	45	92	0.017

Synthesis of silica-coated MNPs ($Fe_3O_4@SiO_2$)

The $Fe_3O_4@SiO_2$ nanoparticles were synthesized by a reverse microemulsion procedure developed by Rossi et al.[25] Triton X-100 (50 g) was dispersed in cyclohexane (500 mL) by sonification. Then, Fe_3O_4 NPs (200 mg, 5.0 mL from a 40 mg mL^{-1} solution in cyclohexane), and ammonium hydroxide (10 mL, 28 wt%) were added, and the mixture was stirred violently at room temperature. After 30 min, tetraethyl orthosilicate (6.0 mL, TEOS) was added drop by drop and the resulting solution was kept under mechanical agitation for 24 h. The resulting products were precipitated with methanol and collected by centrifugation and then washed three times with ethanol. Finally, the product was dried under vacuum at 50 °C overnight.

Synthesis of mercaptopropyl-modified silica-coated MNPs ($Fe_3O_4@SiO_2$-SH)

The functionalization of the $Fe_3O_4@SiO_2$ nanoparticles with ethylenediamine groups was performed by adding mercaptopropyl trimethoxysilane (0.5 mL) to dry toluene (200 mL) that contained $Fe_3O_4@SiO_2$ nanoparticles (500 mg). The resulting solution was heated at reflux for 24 h and then washed with toluene and acetone. The obtained solid material was dried under vacuum at 50 °C for 24 h.

Loading of Pd on mercaptopropyl-modified silica coated MNPs $Fe_3O_4@SiO_2$ SH-Pd^{II}

The above-synthesized $Fe_3O_4@SiO_2$-SH (2.7 g) was mixed with $PdCl_2$ (0.226 g, 1.27 mmol) in dry acetone (150 mL). The mixture was heated at reflux for 24 h under an argon atmosphere. The solid product was filtered by suction, washed three times with acetone, distilled water and acetone successively, and dried at 50 °C under vacuum for 24 h to give the palladium complex $Fe_3O_4@SiO_2$-SH-Pd^{II}. The weight percentage of Pd in the catalyst, as determined by atomic absorption spectroscopic analysis, was 3.81 wt%.

Preparation of the Pd^0 catalyst

The Pd^0 catalyst was prepared by reduction of a Pd^{II} precursor, which was obtained by using $NaBH_4$ in ethanol solution. Typically,

Fe_3O_4@SiO_2-SH-Pd^{II} (100 mg) was added to ethanol (20 mL) that contained $NaBH_4$ (10 mg). Thereafter, the material was washed twice with distilled water and acetone and dried under vacuum.

Typical procedure for the hydrogenation

In a typical experiment, the reagent (1 mmol) was dissolved in ethanol (5 mL) with the catalyst (200 mg) under an H_2 atmosphere. The reaction process was monitored by TLC. After the reaction, the catalyst was separated by a small magnet that was placed at the bottom of the reaction vessel, and conversion was estimated by GC (P.E. AutoSystem XL) or by GC–MS (Agilent 6,890N/5,973N). Thereafter, the catalyst was washed three times with ethanol and dried at room temperature for the next cycle. The catalytic reactions were repeated, and even after 5 cycles there was no deterioration in the catalytic efficiency.

Typical procedure for the carbonylative Suzuki coupling

A mixture of aryl iodide (0.5 mmol), arylboronic acid (0.6 mmol), K_2CO_3 (1.5 mmol), and 1 mol% Pd catalyst in anisole (5 mL) were stirred at 80 °C under a 1 atm pressure of CO. After the reaction, the mixture was cooled to room temperature, separated by magnetic decantation, and the resultant residual mixture was diluted with H_2O (10 mL); this was followed by extraction twice (2×10 mL) with ethyl acetate. The organic fraction was dried over $MgSO_4$, the solvents evaporated under reduced pressure and the residue redissolved in ethanol (5 mL). An aliquot was taken with a syringe and subjected to GC analysis. Yields were calculated against consumption of the aryl iodides.

Acknowledgements

The authors are grateful to the Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization, Gansu Province for financial support.

Keywords: C–C coupling · green chemistry · heterogeneous catalysis · hydrogenation · palladium

[1] a) N. De Kimpe, M. Keppens, G. Froncg, *J. Chem. Soc. Chem. Commun.* **1996**, 635 – 636; b) R. K. Dieter, *Tetrahedron* **1999**, *55*, 4177 – 4236; c) X. J. Wang, L. Zhang, X. Sun, Y. Xu, D. Krishnamurthy, C. H. Senanayake, *Org. Lett.* **2005**, *7*, 5593 – 5595; d) B. Hatano, J. I. Kadokawa, H. Tagaya, *Tetrahedron Lett.* **2002**, *43*, 5859 – 5861.

[2] a) T. Ishiyama, H. Kizaki, T. Hayashi, A. Suzuki, N. Miyaura, *J. Org. Chem.* **1998**, *63*, 4726 – 4731; b) S. Couve-Bonnaire, J. F. Carpentier, A. Mortreux, Y. Castanet, *Tetrahedron Lett.* **2001**, *42*, 3689 – 3691; c) S. Couve-Bonnaire, J. F. Carpentier, A. Mortreux, Y. Castanet, *Tetrahedron* **2003**, *59*, 2793 – 2799.

[3] M. J. Jacinto, O. H. C. F. Santos, R. F. Jardim, R. Landers, L. M. Rossi, *Appl. Catal. A* **2009**, *2*, 117 – 182.

[4] a) H. Azoui, K. Bacsko, S. Cassel, C. Larpent, *Green Chem.* **2008**, *10*, 1197 – 1200; b) D. Sloboda-Rozner, R. Neumann, *Green Chem.* **2006**, *8*, 679 – 681; c) S. V. Jagtap, R. M. Deshpande, *Catal. Today* **2008**, *131*, 353 – 359; d) H. Fu, M. Li, H. Chen, H. Li, *J. Mol. Catal. A-Chem.* **2006**, *259*, 156 – 160; e) C. Fellay, *Chimia* **2007**, *61*, 172 – 174; f) J. Dupont, R. F. De Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667 – 3691.

[5] a) P. McMorn, G. J. Hutchings, *Chem. Soc. Rev.* **2004**, *33*, 108 – 110; b) M. Stasiak, A. Studer, A. Greiner, J. H. Wendorff, *Chem. Eur. J.* **2007**, *13*, 6150 – 6156; c) A. Molnar, B. Rac, *Curr. Org. Chem.* **2006**, *10*, 1697 – 1726; d) J. Mao, X. Hu, H. Li, Y. Sun, C. Wang, Z. Chen, *Green Chem.* **2008**, *10*, 827 – 831; e) A. Amarasekara, I. McNeal, J. Murillo, D. Green, A. Jennings, *Catal. Commun.* **2008**, *9*, 2437 – 2440.

[6] a) A. K. Gupta, A. S. G. Curtis, *J. Mater. Sci. Mater. Med.* **2004**, *15*, 493 – 496; b) T. Neuberger, B. Schoepf, H. Hofmann, M. Hofmann, B. V. Rechenberg, *J. Magn. Magn. Mater.* **2005**, *293*, 483 – 496.

[7] a) B. L. Wang, K. G. Neoh, E. T. Kang, B. Shuter, S.-C. Wang, *Adv. Funct. Mater.* **2009**, *19*, 1 – 8; b) Z. Shi, K. G. Neoh, E. T. Kang, B. Shuter, S.-C. Wang, C. Poh, W. Wang, *ACS Appl. Mater. Interfaces* **2009**, *1*, 328 – 335.

[8] a) J. M. Perez, F. J. Simeone, Y. Saeki, L. Josephson, R. Weissleder, *J. Am. Chem. Soc.* **2003**, *125*, 10192 – 10193; b) D. L. Graham, H. A. Ferreira, P. P. Freitas, *Trends Biotechnol.* **2004**, *22*, 455 – 462.

[9] a) D. Wang, J. He, N. Rosenzweig, Z. Rosenzweig, *Nano Lett.* **2004**, *4*, 409 – 413; b) C. Xu, K. Xu, H. Gu, R. Zheng, H. Liu, X. Zhang, Z. Guo, B. Xu, *J. Am. Chem. Soc.* **2004**, *126*, 9938 – 9939.

[10] a) R. Hiergeist, W. Andra, N. Buske, R. Hergt, I. Hilger, U. Richter, W. Kaiser, *J. Magn. Magn. Mater.* **1999**, *201*, 420 – 422; b) A. Jordan, R. Scholz, P. Wust, H. Fahling, R. Felix, *J. Magn. Magn. Mater.* **1999**, *201*, 413 – 419.

[11] a) A. Corma, P. Concepción, I. Domínguez, V. Forné, M. J. Sabater, *J. Catal.* **2007**, *251*, 39 – 47; b) B. M. Choudary, S. Madhi, N. S. Chowdari, *J. Am. Chem. Soc.* **2002**, *124*, 14127 – 14136; c) G. Wei, W. Q. Zhang, F. Wen, Y. Wang, M. C. Zhang, *J. Phys. Chem. C* **2008**, *112*, 10827 – 10832; d) N. Jamwal, M. Gupta, S. Paul, *Green Chem.* **2008**, *10*, 999 – 1003; e) L. Li, J. L. Shi, J. N. Yan, *Chem. Commun.* **2004**, 1990 – 1991; f) M. J. Gronnow, R. Luque, D. J. Macquarrie, J. H. Clark, *Green Chem.* **2005**, *7*, 552 – 557.

[12] a) U. Laska, C. G. Frost, G. J. Price, P. K. Plucinski, *J. Catal.* **2009**, *268*, 318 – 328; b) N. J. S. Costa, P. K. Kiyohara, A. L. Monteiro, Y. Coppel, K. Philippot, L. M. Rossi, *J. Catal.* **2010**, *276*, 382 – 389; c) F. Zhang, J. Jin, X. Zhong, S. Li, J. Niu, R. Li, J. Ma, *Green Chem.* **2011**, *13*, 1238 – 1243.

[13] a) D. K. Yi, S. S. Lee, J. Y. Ying, *Chem. Mater.* **2006**, *18*, 2459 – 2461; b) B. Panella, A. Vargas, A. Baiker, *J. Catal.* **2009**, *261*, 88 – 93; c) J. Zhang, Y. Wang, H. Ji, Y. Wei, N. Wu, B. Zuo, Q. Wang, *J. Catal.* **2005**, *229*, 114 – 118; d) R. Abu-Reziq, D. Wang, M. Post, H. Alper, *Chem. Mater.* **2008**, *20*, 2544 – 2550.

[14] a) V. Polshettiwar, R. S. Varma, *Org. Biomol. Chem.* **2009**, *7*, 37; b) D.-H. Zhang, G.-D. Li, J.-X. Li, J.-S. Chen, *Chem. Commun.* **2008**, 3414 – 3416.

[15] S. Luo, X. Zheng, J.-P. Cheng, *Chem. Commun.* **2008**, 5719 – 5721.

[16] V. Polshettiwar, R. S. Varma, *Chem. Eur. J.* **2009**, *15*, 1582 – 1586.

[17] X. Feng, G. E. Fryxell, L. Q. Wang, A. Y. Kim, J. Liu, K. M. Kemner, *Science* **1997**, *276*, 923 – 926.

[18] L. Mercier, T. J. Pinnavaia, *Adv. Mater.* **1997**, *9*, 500 – 503.

[19] T. Kang, Y. Park, J. C. Park, Y. S. Cho, J. Yi, *Stud. Surf. Sci. Catal.* **2003**, *146*, 527 – 529.

[20] T. Kang, Y. Park, J. Yi, *Ind. Eng. Chem. Res.* **2004**, *43*, 1478 – 1484.

[21] C. M. Crudden, M. Sateesh, R. Lewis, *J. Am. Chem. Soc.* **2005**, *127*, 10045 – 10050.

[22] C. Diebold, J.-M. Becht, J. Lu, P. H. Toy, C. Le Drian, *Eur. J. Org. Chem.* **2012**, 893 – 896.

[23] L. Wang, J. Bao, L. Wang, F. Zhang, Y. Li, *Chem. Eur. J.* **2006**, *12*, 6341 – 6347.

[24] L.-S. Lin, C. L. Haynes, *Chem. Mater.* **2009**, *21*, 3979 – 3986.

[25] L. M. Rossi, I. M. Nangoi, N. J. S. Costa, *Inorg. Chem.* **2009**, *48*, 4640 – 4642.

Received: March 1, 2012
Revised: April 27, 2012