JOC *Note*

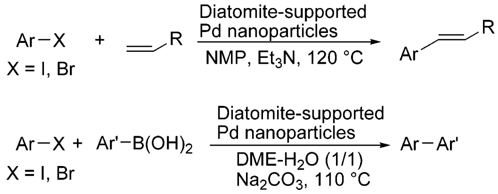
Diatomite-Supported Pd Nanoparticles: An Efficient Catalyst for Heck and Suzuki Reactions

Zuhui Zhang and Zhiyong Wang*

Hefei National Laboratory for Physical Science at Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

zwang3@ustc.edu.cn

Received June 8, 2006



The Pd nanoparticles immobilized on natural diatomite were achieved by a simple procedure. The catalysts are highly active for Heck and Suzuki reactions and can be recovered and reused many times. The catalytic process was also investigated.

Palladium catalysts are often used for versatile transformation in organic synthesis.[1] Many palladium complexes have been used as homogeneous systems in these reactions, but most of them are expensive and air-sensitive. These homogeneous systems always exhibit better activity and selectivity than heterogeneous ones,[2,3] while heterogeneous catalysts have many advantages over their homogeneous counterparts in industrial processes, such as recycling and lower cost. In view of these advantages, many polymer-supported[4] and inorganic solid-supported (e.g., carbon, metal oxides, sol−gel, clays, and zeolites) palladium catalysts[5] have been reported.[6] Diatomite, which is a type of widespread natural porous material, provides a suitable support. Herein, we report a new supported catalyst, in which Pd nanoparticles are immobilized on diatomite, and its application for Heck and Suzuki coupling reactions.

The synthesis of the diatomite-supported Pd nanoparticles was carried out using a slight modification of the procedure previously reported for the synthesis of silver nanoparticles on silica spheres (Scheme 1).[7] Specifically, 200 mg of diatomite was added to 10 mL of water, together with 1 mmol of $SnCl_2 \cdot 2H_2O$ and 3 mmol of CF_3COOH. After the mixture was stirred for 1 h, 200 mg of PVP (poly(vinylpyrrolidone)) and 100 mL of H_2PdCl_4 (2 mM) were added. Then, the supported Pd nanoparticles were achieved by refluxing the above mixture. The transmission electron microscope (TEM) image clearly shows that the Pd nanoparticles were formed with a size in the range of 20−100 nm.[8] The X-ray powder diffraction (XRD) pattern of the diatomite-supported Pd catalyst is consistent with the metallic Pd data in the literature,[9] and no Pd^{2+} was detected, which suggests that the H_2PdCl_4 is completely converted into the metal. X-ray photoelectron spectroscopy (XPS) analyses showed that 3.66 wt % of Pd was found in the diatomite-supported Pd nanoparticles catalyst.

The diatomite-supported Pd prepared above was first used in Heck coupling reactions, which is a versatile method for carbon−carbon bond formation in organic synthesis. The coupling of iodobenzene with methyl acrylate was initially studied as a model reaction. The reaction conditions were systematically optimized, and the results are presented in Table 1. It was found that the best system for the reaction was NMP (1-methylpyrrolidin-2-one) in combination with triethylamine, which delivered a 96% isolated yield of the product **1** within 25 min when 0.1 mol % of diatomite-supported Pd was used (Table 1, entry 5). The catalyst loading could be decreased even further, to 0.01 or 0.001 mol %, when 1.5 or 15 h were required to complete the reaction, respectively (entries 9 and 10; TON

---

(1) (a) Negishi, E. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Wiley: Chichester, UK, 2002. (b) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: Chichester, UK, 2004. (c) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442. (d) Stahl, S. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3400.

(2) For Heck reaction, see: (a) Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989. (b) Shaughnessy, K. H.; Kim, P.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 2123.

(3) For Suzuki reaction, see: (a) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020. (b) Barder, T. E.; Walker, S. D.; Martineli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685.

(4) For recent publications, see: (a) Okamoto, K.; Akiyama, R.; Yoshida, H.; Yoshida, T.; Kobayashi, S. *J. Am. Chem. Soc.* **2005**, *127*, 2125. (b) Dahan, A.; Portnoy, M. *Org. Lett.* **2003**, *5*, 1197. (c) Yang, Y.-C.; Luh, T.-Y. *J. Org. Chem.* **2003**, *68*, 9870. (d) Ooe, M.; Murata, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2004**, *126*, 1604. (e) Garcia-Martinez, J. C.; Lezutekong, R.; Crooks, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 5097. (f) Calò, V.; Nacci, A.; Monopoli, A.; Fornaro, A.; Sabbatini, L.; Cioffi, N.; Ditaranto, N. *Organometallics* **2004**, *23*, 5154. (g) Huang, J.; Jiang, T.; Gao, H.; Han, B.; Liu, Z.; Wu, W.; Chang, Y.; Zhao, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 1397. (h) Parrish, C. A.; Buchwald, S. L. *J. Org. Chem.* **2001**, *66*, 3820. (i) Yamada, Y. M. A.; Takeda, K.; Takahashi, H.; Ikegami, S. *Org. Lett.* **2002**, *4*, 3371. (j) Desforges, A.; Backov, R.; Deleuze, H.; Mondain-Monval, O. *Adv. Funct. Mater.* **2005**, *15*, 1689.

(5) For recent reports, see: (a) Choudary, B. M.; Madhi, S.; Chowdari, N. S.; Kantam, M. L.; Streedhar, B. *J. Am. Chem. Soc.* **2002**, *124*, 14127. (b) Kwon, M. S.; Kim, N.; Park, C. M.; Lee, J. S.; Kang, K. Y.; Park, J. *Org. Lett.* **2005**, *7*, 1077. (c) Mori, K.; Yamaguchi, K.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2002**, *124*, 11572. (d) Yoon, B.; Wai, C. M. *J. Am. Chem. Soc.* **2005**, *127*, 17174. (e) Hagiwara, H.; Sugawara, Y.; Hoshi, T.; Suzukib, T. *Chem. Commun.* **2005**, 2942. (f) Lu, S.-M.; Alper, H. *J. Am. Chem. Soc.* **2005**, *127*, 14776. (g) Djakovitch, L.; Koehler, K. *J. Am. Chem. Soc.* **2001**, *123*, 5990. (h) Pröckl, S. S.; Kleist, W.; Gruber, M. A.; Köhler, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 1881. (i) Dupont, J.; Fonseca, G. S.; Umpierre, A. P.; Fichtner, P. F. P.; Teixeira, S. R. *J. Am. Chem. Soc.* **2002**, *124*, 4228. (j) Hamza, K.; Abu-Reziq, R.; Avnir, D.; Blum, J. *Org. Lett.* **2004**, *6*, 925. (k) Crudden, C. M.; Sateesh, M.; Lewis, R. *J. Am. Chem. Soc.* **2005**, *127*, 10045. (l) González-Arellano, C.; Corma, A.; Iglesias, M.; Sánchez, F. *Adv. Synth. Catal.* **2004**, *346*, 1758.

(6) For recent reviews, see: (a) McNamara, C. A.; Dixon, M. J.; Bradley, M. *Chem. Rev.* **2002**, *102*, 3275. (b) De Vos, D. E.; Dams, M.; Sels, B. F.; Jacobs, P. A. *Chem. Rev.* **2002**, *102*, 3615. (c) Leadbeater, N. E.; Marco, M. *Chem. Rev.* **2002**, *102*, 3217. (d) Astruc, D.; Chardac, F. *Chem. Rev.* **2001**, *101*, 2991. (e) Benaglia, M.; Puglisi, A.; Cozzi, F. *Chem. Rev.* **2003**, *103*, 3401. (f) Fan, Q.-H.; Li, Y.-M.; Chan, A. S. C. *Chem. Rev.* **2002**, *102*, 3385. (g) Bräse, S.; Kirchhoff, J. H.; Köbberling, J. *Tetrahedron* **2003**, *59*, 885.

(7) Kobayashi, Y.; Salgueirino-Maceira, V.; Liz-Marzan, L. M. *Chem. Mater.* **2001**, *13*, 1630.

(8) TEM image and XRD pattern are shown in the Supporting Information.

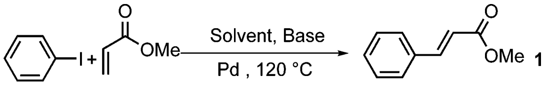
(9) The XRD patterns have three characteristic dihedrals: 40.119, 46.659, and 68.125, with the relative intensities of 100, 60, and 42%, respectively.

10.1021/jo061179k CCC: $33.50 © 2006 American Chemical Society
Published on Web 08/18/2006

SCHEME 1. Preparation of Diatomite-Supported Palladium Nanoparticles

$$\text{Diatomite} \xrightarrow[\text{CF}_3\text{COOH}]{\text{SnCl}_2\cdot 2\text{H}_2\text{O}} \xrightarrow[\text{PVP}]{\text{H}_2\text{PdCl}_4} \text{Diatomite-supported Pd}$$

TABLE 1. Optimization of Base and Solvent for Heck Reaction of Iodobenzene with Methyl Acrylate[a]



entry	base	solvent	Pd (mol %)	time	yield (%)[b]
1	Et_3N	DMF	0.1	40 min	95
2	Et_3N	toluene	0.1	2 h	30
3	Et_3N	CH_3CN	0.1	2 h	53
4	Et_3N	EtOH	0.1	2 h	trace
5	Et_3N	NMP[c]	0.1	25 min	96
6	Et_3N	NMP/H2O (1/1)	0.1	50 min	89
7	NaOAc	NMP	0.1	5 h	49
8	K_2CO_3	NMP	0.1	3 h	38
9	Et_3N	NMP	0.01	1.5 h	96
10	Et_3N	NMP	0.001	15 h	96

[a] Reaction conditions: iodobenzene (1 mmol), methyl acrylate (2 mmol), base (2 mmol), diatomite-supported Pd (0.1 mol %), and 3 mL of solvent at 120 °C. [b] Isolated yield. [c] 1-Methylpyrrolidin-2-one.

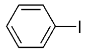
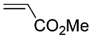
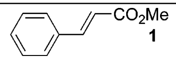
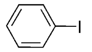
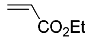
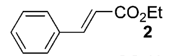
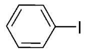
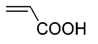
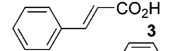
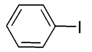
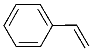
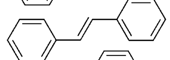
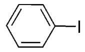
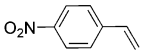
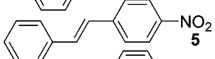
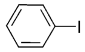
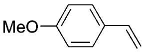
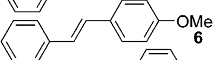
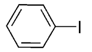
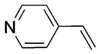
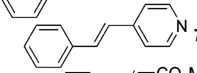
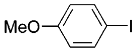
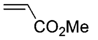
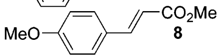
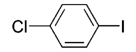
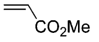
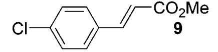
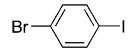
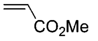
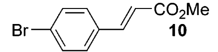
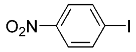
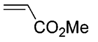
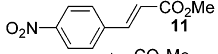
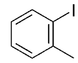
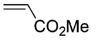
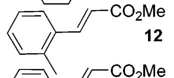
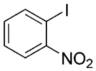
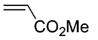
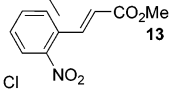
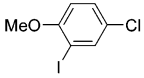
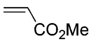
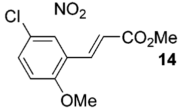
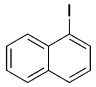
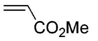
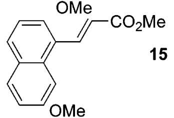
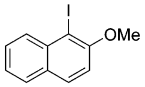
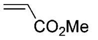
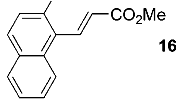
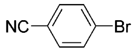
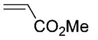
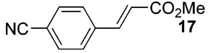
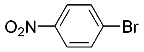
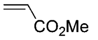
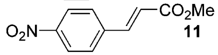
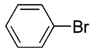
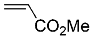
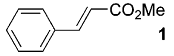
= 9.6 × 10^4 within 15 h in entry 10). With these results in hand, several examples of diatomite-supported palladium-catalyzed Heck coupling of aryl halides with olefins were then tested, and the results are summarized in Table 2. Iodobenzene can react with various alkenes, including acrylate, acrylic acid, styrene, or its derivatives, and gave the corresponding products **1**−**7** with good yields (Table 2, entries 1−7). Besides, these conditions allow for the coupling of both electron-rich and electron-deficient aryl iodides (Table 2, entries 8−16). Notably, the reaction occurred exclusively to aryl iodides in the presence of aryl chloride or aryl bromide as for 1-chloro-4-iodobenzene or 1-bromo-4-iodobenzene (Table 2, entries 9 and 10). Namely, complete chemoselectivities were achieved for the Heck reactions in these cases. Active aryl bromides can undergo the coupling reactions catalyzed by either 0.1 or 1 mol % of Pd to yield similar results with corresponding reaction times (entries 17 and 18). When bromobenzene was used as reactant, 3 mol % of Pd catalysts was required to achieve a similar yield (entry 19).

Furthermore, the diatomite-supported Pd catalyst can also be applied to the Suzuki reaction, another very important methodology for the generation of carbon−carbon bonds, especially applied to the synthesis of biaryls. As listed in Table 3, the conditions tolerated the presence of a wide variety of functional groups, afforded excellent yields of corresponding products **18**−**24** within 1 h starting from either aryl iodides or aryl bromides (Table 3, entry 1−10). Moreover, activated chloride can also give the coupling product with moderate yield in the presence of tetrabutylammonium bromide (TBAB) (Table 3, entry 11).

The feasibility of recycling the diatomite-supported Pd was also examined. In Table 4, we presented the experimental results on the recycling of the supported Pd on a model reaction of iodobenzene with methyl acrylate. After each round, the supported catalyst was recovered by simple centrifugation and used directly for the next round of the reaction without further manipulation. The diatomite-supported Pd exhibited only a marginal loss in activity and required a bit longer time to achieve similar results after the fourth cycle. Even after the sixth round, the supported Pd had a good catalytic activity for this reaction. For large-scale processes, however, it is reasonable to believe that the catalyst can be easily recovered by filtration.

The mechanism of catalytic processes utilizing a heterogeneous palladium source has frequently been disputed in the literature recently.[10] It was proposed that dissolution of palladium species from the surface of the solid support or Pd clusters led to the formation of the active species in solution, and the palladium was redeposited onto the support or Pd clusters after the reaction was finished.[5h,11] The slight loss of catalyst activity after cycles in this case may be due to the loss

TABLE 2. Heck Reaction of Aryl Halides with Olefins[a]

entry	aryl halide	alkene	product	time	yield (%)[d]
1			 **1**	25 min	96
2			 **2**	35 min	95
3			 **3**	30 min	95
4			 **4**	2 h	92
5			 **5**	2 h	94
6			 **6**	4 h	76
7			 **7**	3 h	90
8			 **8**	2.5 h	91
9			 **9**	50 min	96
10			 **10**	30 min	92
11			 **11**	50 min	97
12			 **12**	2 h	95
13			 **13**	2 h	93
14			 **14**	2 h	95
15			 **15**	2 h	96
16			 **16**	2.5 h	91
17			 **17**	16 h 5 h	84 89[b]
18			 **11**	12 h 3 h	86 92[b]
19[c]			 **1**	24 h	85

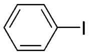
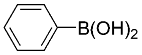
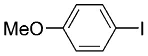
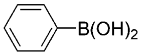
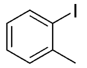
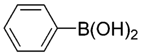
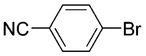
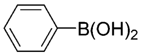
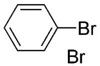
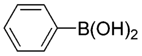
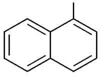
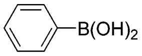
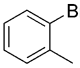
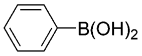
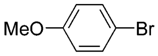
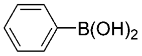
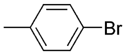
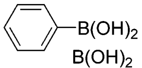
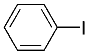
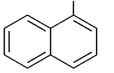
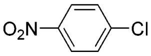
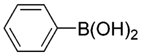
[a] Reaction conditions: ArX (1 mmol), alkene (2 mmol), Et_3N (3 mmol), diatomite-supported Pd (0.1 mol %), and 3 mL of NMP. [b] Diatomite-supported Pd (1 mol %) was used. [c] Diatomite-supported Pd (3 mol %) was used. [d] Isolated yield.

---

(10) For recent reviews on this topic, see: (a) Phan, N. T. S.; Van Der Sluys, M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609. (b) Astruc, D.; Lu, F.; Aranzaes, J. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7852.

TABLE 3. Suzuki Reaction of Aryl Halides with Boronic Acid[a]

$$\mathrm{ArX} + \mathrm{Ar'B(OH)_2} \xrightarrow[\mathrm{DME\text{-}H_2O,\ 110\ ^\circ C}]{\mathrm{Pd,\ Na_2CO_3}} \mathrm{Ar{-}Ar'}$$

entry	halide	boronic acid	product	Pd (mol%)	time	yield (%)[c]
1			**18**	0.1	20 min	95
2			**19**	0.1	60 min	92
3			**20**	0.1	30 min	93
4			**21**	0.1	20 min	97
5			**18**	0.1	30 min	95
6			**22**	1	30 min	93
7			**20**	0.5	30 min	94
8			**19**	1	60 min	88
9			**23**	0.1	25 min	96
10			**22**	0.1	20 min	95
11[b]			**24**	1	120 min	37

[a] Reaction conditions: halide (1 mmol), boronic acid (1.2 mmol), Na_2CO_3 (2 mmol), diatomite-supported Pd (0.1 mol %), and DME/H_2O (1/1). [b] TBAB (0.5 mmol) was used. [c] Isolated yield.

TABLE 4. Recycling of Diatomite-Supported Pd for the Heck Reaction of Iodobenzene with Methyl Acrylate

entry	catalyst	time (min)	isolated yield (%)
1	first cycle	20	96
2	second cycle	20	95
3	third cycle	20	97
4	fourth cycle	20	95
5	fifth cycle	40	96
6	sixth cycle	70	95

of palladium from the support during the reaction. To confirm this assumption, several experiments were then performed. On one hand, with a model reaction of iodobenzene and methyl acrylate, the solid in the reaction mixtures was separated from the hot solutions by filtration after the reaction was completed. The filtrate was then used for the next round, affording conversion of 95% within 40 min, and the Pd content in the filtrate was 8.48 ppm based on elemental analysis of ICP-AES. On the other hand, the supported Pd freshly prepared was placed in NMP at 120 °C for 30 min, and only 2.67 ppm of Pd was detected from the filtrate. This suggested that the oxidation addition of the aryl iodide to the surface Pd^0 converted Pd^0 into Pd^{2+}, resulting in the leaching of a certain amount of palladium particles into the solution. The experimental results showed that the leaching of palladium was necessary for this sustaining catalytic activity, and the diatomite-supported palladium provided the source of palladium in the process. Although the catalytic process involved a homogeneous catalysis, the diatomite-supported palladium, like a catalytic reservoir, is in a different phase from that of reactants and products. This catalytic system has the advantages of both homogeneous and heterogeneous catalysis to some extent. Therefore, it is easy for the catalyst to be reused, and this catalyst has a potential application in industrial scale.

In summary, we presented a new supported catalyst, in which the Pd nanoparticles were immobilized on widespread natural diatomite by a simple procedure which was confirmed by TEM and XRD analyses. The catalyst shows high activity for Heck and Suzuki reactions, and excellent TONs were achieved (TONs up to 9.6×10^4 for the reaction of iodobenzene and methyl acrylate within 15 h) and can be recovered easily and reused many times. This novel supported catalyst is air-stable, and all the reactions can be conducted in air. All these virtues indicate that the diatomite-supported catalyst has a potential application. The studies also reveal that the palladium leaching into the solution during the reaction provides the catalytic site. Further study of the scope of its application is in progress in our laboratory.

Experimental Section

Typical Procedure for the Preparation of Diatomite-Supported Pd Nanoparticles: 200 mg of diatomite was added to 10 mL of water, together with 10 mmol of $SnCl_2 \cdot 2H_2O$ and 30 mmol of CF_3COOH. After the mixture was stirred for 1 h, 100 mL of H_2PdCl_4 (2 mM) and 200 mg of PVP (poly(vinylpyrrolidone)) was added. After the mixture was heated at 110 °C for 2 h, it was cooled to room temperature and filtrated. The catalyst was then obtained by drying the solid under vacuum at 50 °C for 12 h.

General Procedure for the Heck Reaction Catalyzed by Diatomite-Supported Pd: In a 10 mL glass flask were placed aryl halide (1 mmol), alkene (2 mmol), Et_3N (2 mmol), and diatomite-supported Pd (3 mg, 0.1 mol %) in 3 mL of NMP at 120 °C for the appropriate time. The reaction was monitored by TLC, and after completion of the reaction, the mixture was extracted with ethyl acetate three times. The combined organic extracts were dried using anhydrous Na_2SO_4 and evaporated under reduced pressure, and the mixture was then purified by column chromatography over silica gel to afford product with high purity.

General Procedure for the Suzuki Reaction Catalyzed by Diatomite-Supported Pd: In a 10 mL glass flask were placed aryl halide (1 mmol), boronic acid (1.2 mmol), Na_2CO_3 (2 mmol), and diatomite-supported Pd (3 mg, 0.1 mol %) in DME−H_2O (1.5 mL/1.5 mL) at 110 °C for the appropriate time. The reaction was monitored by TLC, and after completion of the reaction, the mixture was extracted with ethyl acetate three times. The combined organic extracts were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure, and the mixture was then purified by column chromatography over silica gel to afford product with high purity.

Acknowledgment. The authors are grateful to the Natural Science Foundation of China (20472078 and 30572234).

Supporting Information Available: TEM image and XRD pattern of the diatomite-supported Pd; characterization data and original ^1H and ^{13}C NMR spectra for products **1**−**24**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO061179K

---

(11) (a) Thathagar, M. B.; ten Elshof, J. E.; Rothenberg, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2886. (b) De Vries, A. H. M.; Mulders, J. M. C. A.; Mommers, J. H. M.; Henderickx, H. J. W.; De Vries, J. G. *Org. Lett.* **2003**, *5*, 3285. (c) Reetz, M. T.; Westermann, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 165.