Heck Reaction Catalyzed by Mesoporous SBA-15-Supported Ionic Liquid–Pd(OAc)$_2$

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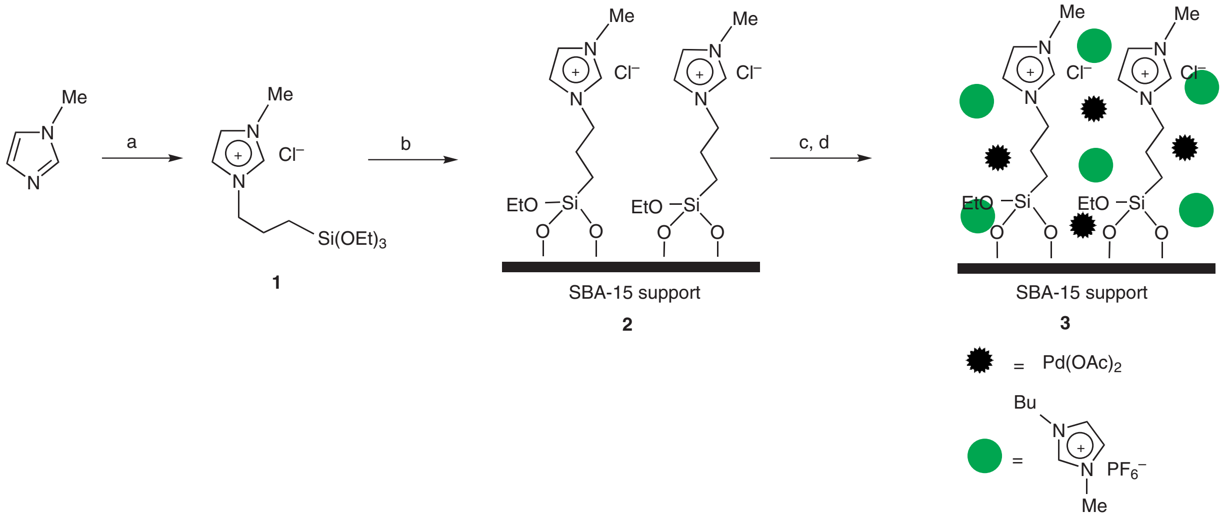
Abstract: Palladium acetate was immobilized into the pores of modified SBA-15 with absorbed ionic liquid. The immobilized catalyst system was studied for Heck coupling. The catalyst exhibited high catalytic activity in the coupling of aryl iodides and activated aryl bromides with acrylates. Moreover, it could be recycled without significant loss of activity.

Key words: Heck reaction, palladium, immobilization, ionic liquid, SBA-15

Heck coupling reaction is one of the most powerful methods for carbon–carbon bond formation in organic synthesis.[1] Most of the Heck reaction proceeds in the presence of palladium catalyst. Considerable efforts have been made for this reaction in order to achieve a high degree of efficiency under mild condition.[2] While palladium catalysts offer widespread utility in the coupling reaction, they are expensive, air-sensitive, and can not be reused continuously in many cases. This limit is of environmental and economic concern in large-scale synthesis. Homogeneous catalysts have been immobilized onto a solid support in order to overcome the limit.[3] Recently, ionic liquids have received much attention as promising media to reuse homogeneous catalysts.[4] However, the reactions which involve ionic liquids as solvents suffer from severe problems related with high cost as well as high viscosity of ionic liquids. It would be desirable to minimize the amount of ionic liquid in a potential process. Search for recyclable, convenient and practical catalytic systems is still a major challenge. In this regard, a new concept of supported ionic liquid phase has been adopted for immobilization of catalysts.[5] Our interest in this area led us to explore the immobilization of palladium acetate with ionic liquid in the channels of mesoporous silica SBA-15. SBA-15 silica has been served as a potential solid support for the immobilization of homogeneous catalysts because of its well-defined, uniform mesopores and facile surface modification.[6] Our strategy is to immobilize an ionic liquid on the pore surface of SBA-15 through the interaction with covalently anchored ionic liquid fragments. In this context, we report the application of SBA-15-supported ionic liquid–palladium acetate matrix for Heck coupling reaction.

First, the surface of SBA-15 was modified with a covalently anchored ionic liquid fragment in order to enhance the interaction between the free ionic liquid and the surface. As shown in Scheme 1, *N*-methylimidazole was reacted with (3-chloropropyl)triethoxysilane to give



Scheme 1 *Reagents and conditions*: (a) (3-chloropropyl)triethoxysilane, 100 °C, 24 h; (b) SBA-15, toluene, reflux; (c) 1-butyl-3-methylimidazolium hexafluorophosphate, Pd(OAc)$_2$, THF, r.t., 1 h; (d) removal of THF.

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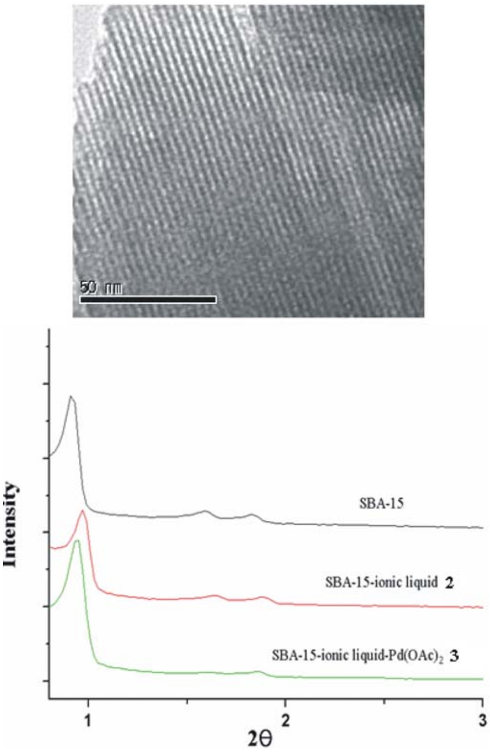


Figure 1 TEM image of **3** and XRD pattern of **2** and **3**

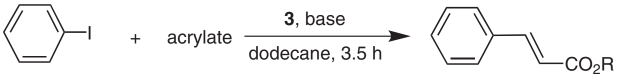
N-1-(3-triethoxysilylpropyl)-3-methylimidazolium chloride (**1**).[7] SBA-15-supported ionic liquid **2** was prepared by treatment of SBA-15 with an excess amount of *N*-1-(3-triethoxysilylpropyl)-3-methylimidazolium chloride in refluxing toluene.[8] Both nitrogen analysis and weight gain confirm the incorporation of ionic liquid **1**, giving modified SBA-15 **2** with loading ratio of 1.05 mmol/g. Next, immobilization of palladium acetate–ionic liquid on the surface of the pore walls was performed by immersing the modified SBA-15 **2** in THF solution of palladium acetate and ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, followed by removing THF from the mixture.[9] In addition, palladium acetate and the ionic liquids are very miscible in THF and less soluble in nonpolar solvents and water. A weight composition of 0.06 $Pd(OAc)_2$/0.1 ionic liquid/1.0 modified SBA-15 silica **2** was used. The Pd content of 0.21 mmol/g was measured by inductively coupled plasma (ICP) analysis. The absorbed ionic liquid spreads as multiple layers of free ionic liquid in the pores of SBA-15 support. Palladium acetate in the ionic liquid layer would act like a homogeneous catalyst. Therefore, this system may possess the advantages of both homogeneous and heterogeneous catalysts.

The HRTEM image of modified SBA-15 **3** is very similar to symmetry of the pore arrays (Figure 1). It reveals that the hexagonal symmetry of the pore arrays is still conserved after the immobilization of ionic liquid–palladium acetate matrix onto the modified SBA-15. This mesoporous character is also confirmed by XRD (Figure 1). Apparently, there is less change of the lattice parameters upon the immobilizing process. The BET surface area, total pore volume and pore diameter of SBA-15 materials are listed in Table 1. Mesoporous SBA-15 used as a support has high surface area of 750 m^2/g and mesopore diameter of 8.33 nm. As expected, the surface area, total pore volume and pore diameter of the functionalized SBA-15 decreased dramatically from those of parent SBA-15 because of the grafting of organic species on the surface of the mesopores. Mesoporous SBA-15 may be a suitable support in the development of supported ionic liquid catalysis.

Table 1 Textural Properties Determined from Nitrogen Adsorption Experiments at 77 K

	Specific BET surface area (m^2/g)	Total pore volume (cm^3/g)	Mesopore diameter (nm)	Loading (mmol/g)
SBA-15	750	0.83	8.33	–
2	334	0.61	7.35	1.05
3	215	0.38	7.09	0.21

Table 2 Heck Reaction of Iodobenzene with Acrylates in the Presence of Catalyst **3**[a]

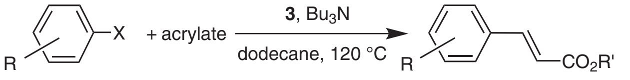


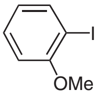
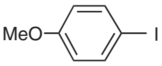
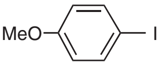
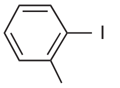
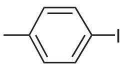
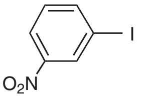
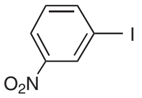
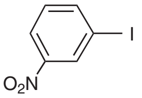
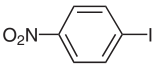
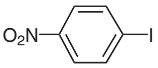
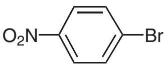
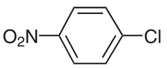
Entry	Acrylate[b]	Base	Temp (°C)	Yield (%)[c]
1	MA	Bu_3N	130	100 (98)
2	EA	Bu_3N	130	100 (99)
3	BA	Bu_3N	130	100 (96)
4	MA	Bu_3N	120	98
5	EA	Bu_3N	120	99
6	BA	Bu_3N	120	98
7	BA	Bu_3N	110	84 (82)
8	MA	$(i\text{-Pr})_2EtN$	120	80
9	EA	$(i\text{-Pr})_2EtN$	120	82
10	MA	Et_3N	120	71

[a] Reaction conditions: iodobenzene (1.0 mmol), acrylate (1.3 mmol), base (1.5 mmol), **3** (1.0 mol%), dodecane (1.3 mL).
[b] MA = methyl acrylate, EA = ethyl acrylate, BA = butyl acrylate.
[c] Determined by GC analysis. Isolated yield is given in parenthesis.

The catalytic activity of the immobilized $Pd(OAc)_2$ was investigated in Heck coupling reaction.[10] We tested the coupling of iodobenzene with acrylate in dodecane as a model reaction (Table 2). In our initial experiments, the coupling of iodobenzene with methyl acrylate was carried out in the presence of 1.0 mol% of **3** and Bu_3N as a base. The reaction was complete at 130 °C in 3.5 hours. Quantitative conversions were also observed in the couplings with ethyl acrylate and butyl acrylate (entries 2 and 3).

Table 3 Heck Reaction of Aryl Halides with Acrylates in the Presence of Catalyst **3**[a]



Entry	Aryl halide	Acrylate[b]	Time (h)	Yield (%)[c]
1		MA	5	83 (81)
2		MA	3	98 (95)
3		BA	3	94
4		MA	5	84 (80)
5		MA	5	87 (83)
6		MA	3	94
7		MA	3	100 (99)
8		EA	3	99
9		BA	3	97
10		MA	2	100 (99)
11		BA	2	100
12		MA	5	97 (94)
13		BA	12	21

[a] Reaction conditions: aryl halide (1.0 mmol), acrylate (1.3 mmol), Bu_3N (1.5 mmol), **3** (1.0 mol%), dodecane (1.3 mL).

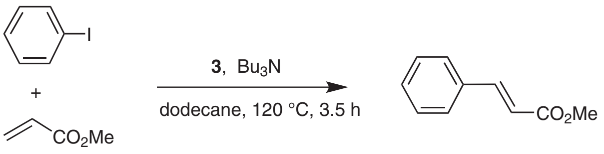
[b] MA = methyl acrylate, EA = ethyl acrylate, BA = butyl acrylate.

[c] Determined by GC analysis. Isolated yield is given in parenthesis.

The catalytic activity was not significantly decreased at 120 °C (entries 4–6). The turnover frequency (TOF) was as high as 29 h^{-1} for the coupling. In contrast, the reaction was somewhat slow at 110 °C (entry 7). Lower yields were obtained when i-Pr_2EtN or Et_3N was used as a base (entries 8–10).

In order to extend the scope of our catalytic system, we next performed Heck reaction of substituted iodobenzene with acrylates. As shown in Table 3, catalyst **3** showed outstanding activities in the coupling of deactivated aryl iodides such as 2-iodoanisole, 4-iodoanisole, 2-iodotoluene and 4-iodophenol (entries 1–6) as well as activated 1-iodo-4-nitrobenzene and 1-iodo-3-nitrobenzene (entries 7–11). Deactivated aryl iodides possessing electron-donating groups showed a slight drop in reactivity compared to those possessing electron-withdrawing groups. A little longer reaction time was required to reach a satisfactory conversion. High reactivity was still observed in the coupling of activated 1-bromo-4-nitrobenzene (entry 12). However, an attempt to couple 1-chloro-4-nitrobenzene was not successful (entry 13).

Table 4 Reusability of Catalyst **3** over Six Runs



Recycle	1st	2nd	3rd	4th	5th	6th
Yield (%)	100	100	98	98	99	99

The recycling of catalyst is an important issue in the heterogeneous reaction. Thus, we turned our attention to the reusability of our catalyst **3**. The catalyst was recovered by a simple filtration and reused in the reaction of iodobenzene with methyl acrylate. The reusability of **3** was demonstrated by conducting six runs without considerable loss of catalytic activity (Table 4). Furthermore, ICP analysis of the solution indicated that less Pd metal (< 0.1 ppm) leached into the reaction solution. This excellent reusability and high stability of the catalyst would be explained by strong binding of $Pd(OAc)_2$ to SBA-15-supported ionic liquid and site isolation, that is, the absence of interactions between catalytic sites, which causes aggregation of the Pd complex and formation of less active Pd catalyst. The successful recycling allows for a more economic and environmentally friendly process.

In summary, palladium acetate with ionic liquid was successfully confined onto modified SBA-15 silica. We have shown that the immobilized palladium acetate can be efficiently used as a recyclable catalyst for Heck reaction. Moreover, SBA-15 was proven to be an excellent support for the supported ionic liquid catalysis. Further studies of other reactions are currently in progress.

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References and Notes

(1) Reviews: (a) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009. (b) Amatore, C.; Jutand, A. *Acc. Chem. Rev.* **2000**, *33*, 314. (c) Zapf, A. *Angew. Chem. Int. Ed.* **2003**, *42*, 5394. (d) Trzeciak, A. M.; Ziółkowski, J. J. *Coord. Chem. Rev.* **2005**, *249*, 2308.

(2) (a) Tulloch, A. A. D.; Danopoulos, A. A.; Cafferkey, S. M.; Kleinhenz, S.; Hursthouse, M. B.; Tooze, R. P. *Chem. Commun.* **2000**, 1247. (b) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741. (c) Reddy, K. R.; Surekha, K.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **2000**, *19*, 2637. (d) Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290. (e) Lee, H. M.; Zeng, J. Y.; Hu, C.-H.; Lee, M.-T. *Inorg. Chem.* **2004**, *43*, 6822. (f) Devasher, R. B.; Moore, L. R.; Shaughnessy, K. H. *J. Org. Chem.* **2004**, *69*, 7919. (g) Sliger, M. D.; Broke, G. A.; Shaughnessy, K. H. *J. Organomet. Chem.* **2005**, *690*, 1478. (h) Pascu, S. I.; Coleman, K. S.; Cowley, A. R.; Green, M. H.; Rees, N. H. *J. Organomet. Chem.* **2005**, *690*, 1645. (i) Smith, R. C.; Bodner, C. R.; Earl, M. J.; Sears, N. C.; Hill, N. E.; Keles, M.; Aydin, Z.; Serindag, O. S. *J. Organomet. Chem.* **2007**, *692*, 1951. (j) Scrivanti, A.; Bertoldini, M.; Matteoli, U.; Beghetto, V.; Antonaroli, S.; Marini, A.; Crociani, B. *J. Mol. Catal. A: Chem.* **2005**, *235*, 12. (k) Taige, M. A.; Zeller, A.; Ahrens, S.; Goutal, S.; Herdtweck, E.; Strassner, T. *J. Organomet. Chem.* **2007**, *692*, 1519. (l) Nonnenmacher, M.; Kunz, D.; Rominger, F.; Oeser, T. *J. Organomet. Chem.* **2007**, *692*, 2554.

(3) (a) Bandini, M.; Luque, R.; Budarin, V.; Macquarrie, D. J. *Tetrahedron* **2005**, *61*, 9860. (b) Mingji, D.; Liang, B.; Wang, C.; You, Z.; Xiang, J.; Dong, G.; Chen, J.; Yang, Z. *Adv. Synth. Catal.* **2004**, *346*, 1669. (c) Papp, A.; Galbács, G.; Molnár, A. *Tetrahedron Lett.* **2005**, *46*, 7725. (d) Polshettiwar, V.; Varma, R. S. *Tetrahedron* **2008**, *64*, 4637. (e) Dawood, M. K. *Tetrahedron* **2007**, *63*, 9642. (f) Tandukar, S.; Sen, A. *J. Mol. Catal. A: Chem.* **2007**, *268*, 112.

(4) (a) Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed.* **2000**, *39*, 3773. (b) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667. (c) Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. *Tetrahedron* **2005**, *61*, 1015. (d) Akiyama, T.; Suzuki, A.; Fuchibe, K. *Synlett* **2005**, 1024. (e) Ranu, B. C.; Banerjee, S.; Jana, R. *Tetrahedron* **2007**, *63*, 776.

(5) (a) Mehnert, C. P.; Cook, R. A.; Dispenziere, N. C.; Afeworki, M. *J. Am. Chem. Soc.* **2002**, *124*, 12932. (b) Breitenlechner, S.; Fleck, M.; Müller, T. E.; Suppan, A. *J. Mol. Catal. A: Chem.* **2004**, *214*, 175. (c) Mehnert, C. P. *Chem. Eur. J.* **2005**, *11*, 50. (d) Hagiwara, H.; Sugawara, Y.; Isobe, K.; Hoshi, T.; Suzuki, T. *Org. Lett.* **2004**, *6*, 2325.

(6) (a) Zhao, D.; Huo, Q.; Feng, J.; Chemlka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024. (b) Wight, A. P.; Davis, M. E. *Chem. Rev.* **2002**, *102*, 3586. (c) Du, G.; Lim, S.; Pinault, M.; Wang, C.; Fang, F.; Pfefferle, L.; Haller, G. L. *J. Catal.* **2008**, *253*, 74.

(7) (a) Gadenne, B.; Hesemann, P.; Moreau, J. J. E. *Chem. Commun.* **2004**, 1768. (b) Brenna, S.; Posset, T.; Furrer, J.; Blumel, J. *Chem. Eur. J.* **2006**, *12*, 2880.

(8) **Modification of SBA-15 with Ionic Liquid**: To a solution of *N*-1-(3-triethoxysilylpropyl)-3-methylimidazolium chloride (0.77 g, 2.4 mmol) in toluene was added SBA-15 (2.0 g). The mixture was stirred at 105 °C for 12 h. After cooling, the reaction mixture was filtered and washed completely with CH_2Cl_2, and dried at 90 °C under vacuum to yield modified SBA-15 **2** (2.48 g). Elemental analysis and weight gain showed that 1.05 mmol of the ionic liquid was anchored on 1.0 g of **2**.

(9) **Immobilization of $Pd(OAc)_2$ onto Modified SBA-15 2**: To a stirred solution of $Pd(OAc)_2$ (60 mg, 0.4 mmol) and 1-butyl-3-methylimidazolium hexafluorophosphate (100 mg, 0.42 mmol) in THF (10 mL), modified SBA-15 **2** (1.0 g, 1.05 mmol/g) was added. The mixture was stirred for 1 h at r.t., and then THF was removed under reduced pressure. The resulting powder was dried under vacuum at 90 °C to give SBA-15-supported ionic liquid–$Pd(OAc)_2$ **3** (1.15 g). ICP analysis showed that 0.21 mmol of Pd was immobilized on 1.0 g of **3**.

(10) **General Procedure for the Heck Reaction**: Reaction was carried out in a 5-mL glass vial equipped with a Teflon screw cap. A mixture of aryl halide (1.0 mmol), acrylate (1.3 mmol), Bu_3N (1.5 mmol), and catalyst **3** (1.0 mol%) in dodecane (1.5 mL) was stirred at 120 °C. The reaction was periodically monitored by GC analysis. The mixture was diluted with Et_2O (15 mL) and H_2O (3 mL). Catalyst **3** was separated from the mixture and washed with H_2O and Et_2O. The ethereal layer was dried over $MgSO_4$ and then evaporated under reduced pressure. The residue was purified by column chromatography on silica gel.