

Palladium acetate immobilized in a hierarchical MFI zeolite-supported ionic liquid: a highly active and recyclable catalyst for Suzuki reaction in water

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Palladium acetate was immobilized in thin ionic liquid layers on the mesopore wall of hierarchical MFI zeolite, and tested as a catalyst for Suzuki coupling reaction in water. The catalyst exhibited very high activity in the coupling of various aryl bromides with arylboronic acids. Moreover, the catalyst could be recycled without a significant loss of catalytic activity.

Introduction

Suzuki coupling of aryl halides with arylboronic acids has served as a powerful reaction for the construction of biaryl units in organic synthesis.¹ Various kinds of homogeneous palladium catalysts are used for the Suzuki reaction.² One practical limit to performing homogeneously catalyzed reactions is the difficulty of separating the product from the catalyst or removing the product continuously. This limit is of environmental and economic concern in large scale-synthesis. Homogeneous catalysts are often immobilized in a porous inorganic or organic support in order to overcome these problems facing green chemistry.^{3,4} Recently, ionic liquids have received much attention as promising green media to reuse homogeneous catalysts.⁵ However, the reactions which involve ionic liquids as solvents suffer from severe problems related with expensive cost and high viscosity of the ionic liquids. It would be desirable to minimize the amount of ionic liquid in a potential process. In this regard, a new concept of a supported ionic liquid phase has been adopted for immobilization of catalysts.⁶ This strategy is to physically coat an ionic liquid containing homogeneous catalyst as a thin film on the surface of a solid support, which leads to a significant decrease in the amount of ionic liquid as well as a large increase in the contact area between the two phases. Recently, Hagiwara *et al.* have demonstrated that the ionic liquid layer can be stabilized when amino groups are grafted on the surface of silica support.^{6d} Research for efficient, convenient and recyclable catalytic systems based on supported ionic liquids is still a major challenge. Our interest in this area has prompted us to explore immobilization of palladium acetate with ionic liquid in the mesoporous channels of a hierarchically porous MFI zeolite. In addition to the use of the acidic hierarchical zeolite, our

approach is to effectively immobilize the ionic liquid layer by covalently grafting ionic liquid molecules on the surface of the mesopore walls.

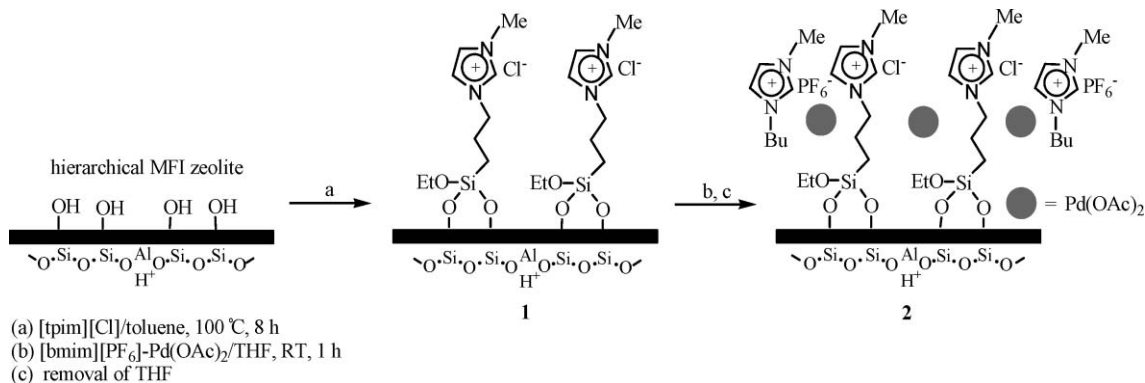
Previously, Ryoo and co-workers have developed a synthesis route to the highly mesoporous, hierarchically porous zeolites, which can serve as a potentially new support for the immobilization of homogeneous catalysts.⁷ In the case of hierarchical MFI zeolite, the mesopore diameters are uniform and tailored, typically in the range of 3–10 nm. The mesopore walls are made of crystalline microporous zeolite frameworks. The zeolite frameworks are terminated at the surface of mesopore walls with a high concentration of silanol groups. Through condensation of the silanol groups with organosilanes, the mesopore walls can be easily functionalized with organic groups. In particular, the functionalized MFI zeolite with a crystalline zeolite framework exhibited higher hydrothermal stability than other mesoporous materials without crystalline framework such as SBA-15 and MCM-41.⁸

As shown in Scheme 1, the immobilization of palladium acetate in the present work was performed in two steps. A hierarchical MFI zeolite with a narrow distribution of mesopore diameters around 3.3 nm was hydrothermally synthesized using dodecyltrimethyl[3-(trimethoxysilyl)propyl]ammonium chloride as a mesopore-directing agent.⁹ The hierarchical zeolite had the specific BET surface area of 502 m²/g and pore volume of 0.46 cm³/g. Mesopore walls of the MFI zeolite **1** were functionalized by the treatment with 1-(3-triethoxysilylpropyl)-3-methylimidazolium chloride ([tpim][Cl])¹⁰ in refluxing toluene. Loading of the imidazolium ionic liquid could be increased up to 1.3 mmol/g. The functionalization capacity was higher than those for amorphous silica gel¹¹ (0.87 mmol/g) and SBA-15 mesoporous silica¹² (1.0 mmol/g) under the same treatment conditions. The MFI zeolite has an approximately two times smaller surface area of the mesopore walls than SBA-15. Thus, the surface functionalization density should be at least two times higher at the mesopore walls of the hierarchical zeolite than SBA-15. The high density of surface functionalization in the case of hierarchical zeolite seemed to be due to densely populated silanol groups that were available on the mesopore walls.⁸ Such a mesoporous material may be a preferable choice in the development of supported ionic liquid catalysts because the covalently grafted ionic liquid moieties in a high density are supposed to immobilize free ionic liquid with catalytic species effectively.

In the second step for immobilization, the modified zeolite **1** (1.1 mmol/g) was immersed in a THF solution containing ionic liquid 1-butyl-3-methylimidazolium hexafluorophos-

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Scheme 1 Preparation of MFI-supported Pd(OAc)₂-ionic liquid.

phate ([bmim][PF₆])¹³ and Pd(OAc)₂. Their weight ratio was 0.07 Pd(OAc)₂/0.14 ionic liquid/1.0 modified MFI zeolite **1**. The THF solvent was removed by evaporation, and the zeolite sample was washed with diethyl ether. The ether washing was to remove weakly adsorbed Pd(OAc)₂ without loss of the insoluble [bmim][PF₆]. Inductively coupled plasma (ICP) emission analysis showed a Pd content of 0.24 mmol/g in the resultant sample, in good agreement with the initial loading. This is similar to the strategy of Hagiwara *et al.* who grafted amino groups on silica gel.^{6d} In contrast, we grafted ionic liquid moieties on the mesopore walls of the zeolite. We believe that the added Pd(OAc)₂-[bmim][PF₆] matrix can be strongly incorporated into the covalently grafted ionic liquid layer through the interaction between the free ionic liquid and the grafted ionic liquid moiety. Transmission electron microscopic (TEM) and scanning electron microscopic (SEM) images showed that the resultant sample **2** is very similar to that of the parent MFI (Fig. 1).

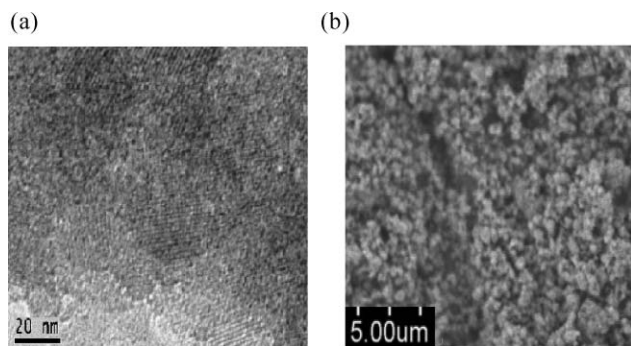


Fig. 1 (a) TEM image and (b) SEM image of MFI-IL-Pd(OAc)₂ **2**.

The heterogeneous Suzuki coupling has been mainly studied with reactive but expensive aryl iodides. The use of aryl bromides instead of aryl iodides would be more desirable for the large-scale applications. Suzuki coupling is generally performed in an organic solvent or water-organic mixture. The use of water as a safe and environmentally sustainable reaction medium has attracted much attention due to increasing environmental concerns in recent years. We tested the coupling of 4-bromoanisole with phenylboronic acid in water as a model reaction (Table 1). The reaction was initially performed using 0.3 mol% of catalyst **2** and K₃PO₄ as base in neat water.

Table 1 Suzuki coupling of 4-bromoanisole with phenylboronic acid in water^a

Entry	2 (mol%)	TBAB	<i>T</i> (°C)	Time (h)	yield ^b (%)
1	0.3	0	95	5.0	90 (92)
2	0.3	0.2	65	0.7	90 (93)
3	0.3	0.4	65	0.5	96 (99)
4	0.3	0.6	65	0.5	97 (99)
5 ^c	0.3	0.4	65	0.5	91 (96)
6 ^d	0.3	0.4	65	0.5	91 (95)
7	0.1	0.4	65	0.5	94 (98)
8	0.05	0.4	65	0.5	92 (96)
9	0.3	0.4	40	1.5	90 (95)
10	0.1	0.4	40	2.5	87 (92)

^a Molar ratio: bromobenzene (1.0 equiv.), phenylboronic acid (1.1 equiv.), **2** (0.3–0.05 mol%), Pd loading ratio: 0.24 mmol/g, and K₃PO₄ (2.0 equiv.). ^b Isolated yields (GC yield in parenthesis). ^c Na₂CO₃ was used instead of K₃PO₄. ^d Cs₂CO₃ was used instead of K₃PO₄.

High conversion was obtained at 95 °C in 5 h (entry 1). A phase transfer agent, tetrabutylammonium bromide (TBAB), was added to enhance the reactivity of the reaction. The TBAB effect on catalytic activity was surveyed with different amounts of TBAB (entries 2–4). The biphasic coupling reaction was found to be very efficient in the presence of 0.4 equiv. of TBAB. 4-Bromoanisole could be cleanly coupled with phenylboronic acid in 99% yield within a very short reaction time. Use of Na₂CO₃ or Cs₂CO₃, instead of K₃PO₄ resulted in slightly less effective coupling (entries 5 and 6). It is remarkable that high reactivity could be observed at a very low catalyst loading of 0.1–0.05 mol% (entries 7 and 8). The turnover frequency (TOF) was as high as 3840 h⁻¹ for the coupling. It is also noteworthy that catalyst **2** shows outstanding performance even at a low temperature of 40 °C (entries 9 and 10).

In order to investigate the scope on aryl bromides in the coupling with phenylboronic acid, different aryl bromides were employed in the reaction (Table 2). High catalytic activity for both bromobenzene and deactivated aryl bromides such as 2-bromotoluene, 4-bromotoluene, and 2-bromoanisole was observed, affording the corresponding biphenyl compounds in excellent yields (entries 1–5). Activated 4-bromoacetophenone, 1-bromo-4-nitrobenzene and 1-bromo-3-nitrobenzene were

Table 2 Suzuki coupling of aryl bromide with phenylboronic acid in water^a

Entry	Aryl bromide	Time (h)	T (°C)	Yield ^b (%)
1		0.5	65	95 (97)
2		0.7	65	88 (92)
3		2	50	87 (92)
4		0.7	65	85 (90)
5		0.5	65	93 (94)
6		0.3	65	95 (100)
7		0.4	65	98 (100)
8		0.4	65	97 (100)
9		2.0	RT	94 (98)
10		3.0	RT	97 (97)
11		1.2	95	85 (91)
12 ^c		0.5	65	71 (75)
13 ^c		0.7	65	72 (79)
14 ^c		1.2	95	51 (53)

^a Unless otherwise noted, reaction was run employing aryl bromide (1.0 equiv.), phenylboronic acid (1.1 equiv.), **2** (0.3 mol%), TBAB (0.4 equiv.) and K₃PO₄ (2.0 equiv.). ^b Isolated yields (GC yield in parenthesis). ^c Reaction was carried out in the presence of Pd(OAc)₂ instead of **2**.

rapidly coupled at 65 °C or even room temperature in quantitative yields (entries 6–10). Activated aryl bromides possessing electron-withdrawing groups showed higher reactivity than those possessing electron-donating groups. A slightly shorter reaction time was required to reach almost quantitative conversion. It should be noted that sterically hindered 2-bromo-

1,3-dimethylbenzene could be coupled in high yield (entry 11). For comparison, unsupported Pd(OAc)₂ was tested as catalyst under the same reaction conditions (entries 12–14). Comparison of entries 2 vs. 12, 4 vs. 13, and 11 vs. 14 indicated that the supported catalyst **2** was superior to unsupported Pd(OAc)₂. A more significant difference was observed in the coupling of less reactive 2-bromo-1,3-dimethylbenzene with steric hindrance. The results indicate that the use of a supported ionic liquid system is beneficial in enhancing the reactivity. The high efficiency of catalyst **2** is probably attributed to the fact that Pd(OAc)₂ is well-spread in the ionic liquid phase, and therefore more readily accessible for the reactants. Moreover, the anchored ionic liquid induces the formation of a hydrophobic environment on the surface of the MFI zeolite.

The catalytic system was further extended to the coupling reaction of aryl bromides with different arylboronic acids (Table 3). The results show that the catalytic system is very efficient for Suzuki coupling reaction of aryl bromides with different arylboronic acids. Deactivated aryl bromides could react with electron-rich 4-methylphenylboronic acid, and 4-methoxyphenylboronic acid afforded the corresponding products with high yields (entries 1–8). Besides, these conditions allow for the coupling of the deactivated aryl bromides with electron-deficient 4-chlorophenylboronic acid, 2-chlorophenylboronic acid, and 3-nitrophenylboronic acid (entries 9–17). Nearly complete conversions were also achieved for the reactions within short reaction times. The sterically hindered 2-bromo-1,3-dimethylbenzene could undergo coupling reactions with different arylboronic acids catalyzed by only 0.3 mol% of **2** to yield similar results, although a higher temperature and longer time were required (entries 18 and 19). The catalytic system was applicable to a wide range of arylboronic acids in all cases.

We turned our attention to the reusability of our catalyst. The recycling of the catalyst is an important issue in the heterogeneous reaction. As we described above, the major advantages of immobilized catalyst is its easy recovery by filtration or centrifugation. The recycling of **2** was investigated by the coupling of 4-bromoanisole and 1-bromo-4-nitrobenzene with phenylboronic acid in water. As shown in Table 4, the catalyst could be recovered and reused five times without significant loss of activity. Furthermore, ICP analysis of the solution indicated that less Pd metal (1.5 ppm) leached into the reaction solution during the first run. The isolated solution did not exhibit any further reactivity. This excellent reusability and high stability of the catalyst would be explained by strong binding of Pd(OAc)₂ to MFI-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. In addition to the high activity, the successful recycling of this catalytic system allows for a more economic and environmentally friendly process.

Experimental

Synthesis of hierarchical MFI zeolite

Hierarchical MFI zeolite was hydrothermally synthesized with dodecyltrimethyl[3-(trimethoxysilyl)propyl]ammonium chloride

Table 3 Suzuki coupling of aryl bromide with arylboronic acid in water^a


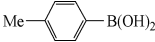
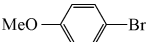
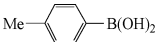
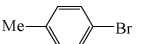
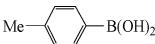

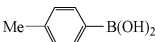

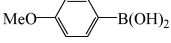
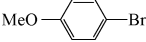
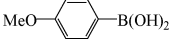
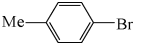
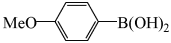

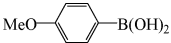

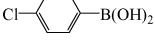
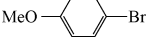
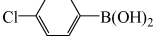
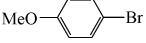
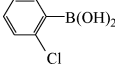

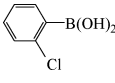

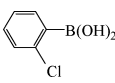

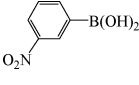
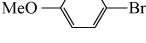
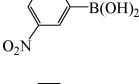
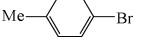
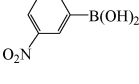

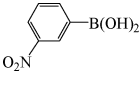

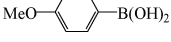
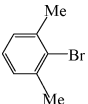
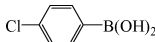
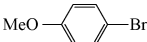
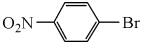
Entry	Aryl bromide	Arylboronic acid	Time (h)	Yield ^b (%)
1			0.5	94 (95)
2			0.5	92 (95)
3			1.0	95 (97)
4			0.5	91 (96)
5			0.5	94 (95)
6			0.5	91 (96)
7			1.0	91 (97)
8			0.5	93 (97)
9			0.5	95 (96)
10			0.5	93 (92)
11			0.5	90 (93)
12			2.0	85 (90)
13			1.0	87 (91)
14			0.5	96 (98)
15			0.5	96 (99)
16			0.5	92 (96)
17			0.5	92 (97)
18 ^c			2.5	84 (90)

Table 3 (Contd.)

Entry	Aryl bromide	Arylboronic acid	Time (h)	Yield ^b (%)
19 ^c			2.5	85 (91)

^a Unless otherwise noted, reaction was run employing aryl bromide (1.0 equiv.), arylboronic acid (1.1 equiv.), **2** (0.3 mol%), TBAB (0.4 equiv.) and K₃PO₄ (2.0 equiv.) at 65 °C. ^b Isolated yields (GC yield in parenthesis). ^c Reaction temp. was 90 °C.

Table 4 Recycling of catalyst **2** in Suzuki coupling of aryl bromide with phenylboronic acid^a

Aryl halide	Cycle	Yield ^b (%)	Cycle	Yield ^b (%)
	1	99	4	96
	2	97	5	96
	3	98		
	1	100	4	99
	2	100	5	99
	3	100		

^a Reaction was carried out using aryl bromide (1.0 equiv.), phenylboronic acid (1.1 equiv.), **2** (0.3 mol%), TBAB (0.4 equiv.) and K₃PO₄ (2.0 equiv.) at 65 °C for 0.5 h. ^b GC yield.

as a mesopore-directing agent.⁹ The product was dried in an oven at 373 K and subsequently calcined in air at 823 K. The sample was ion-exchanged into the NH₄⁺ form by repeating the ion-exchange treatment three times with a 1 M aqueous solution of NH₄NO₃ at 353 K for 4 h. The zeolite was calcined at 823 K for 6 h to convert it to the H⁺ form.

Modification of the surface of MFI zeolite with ionic liquid

To a solution of 1-(3-triethoxysilylpropyl)-3-methylimidazolium chloride (1.0 g, 3.1 mmol) in toluene was added MFI zeolite (2.0 g). The mixture was stirred at 100 °C for 10 h. After cooling, the reaction mixture was filtered and washed with CH₂Cl₂ several times, and dried at 60 °C under vacuum to yield MFI zeolite-supported ionic liquid **1** (2.57 g). Elemental analysis and weight gain showed that 1.2 mmol of 1-(3-triethoxysilylpropyl)-3-methylimidazolium chloride was anchored on 1.0 g of **1**.

Immobilization of Pd(OAc)₂-ionic liquid onto modified MFI zeolite

To a stirred solution of Pd(OAc)₂ (66 mg, 0.29 mmol) and 1-butyl-3-methylimidazolium hexafluorophosphate (165 mg, 0.58 mmol) in THF (10 mL), modified MFI zeolite **1** (1.0 g, 1.20 mmol/g) was added. The mixture was stirred for 40 min at room temperature, and then THF was slowly removed under reduced pressure. The resulting powder was washed with diethyl ether and dried under vacuum at 60 °C to give MFI zeolite-supported Pd(OAc)₂-ionic liquid **2** (1.21 g). The Pd content of

0.22 mmol/g was measured by inductively coupled plasma (ICP) analysis.

General procedure for heterogeneous Suzuki reaction

Aryl halide (1.0 mmol), phenylboronic acid (134 mg, 1.1 mmol), K_3PO_4 (424 mg, 2.0 mmol), TBAB (129 mg, 0.4 mmol), dodecane (40 mg, internal standard) and catalyst **2** (13.5 mg, 0.22 mmol/g, 0.3 mol%) were mixed in H_2O (3.0 mL). The mixture was stirred at 65 °C in an air atmosphere. The crude was analysed by GC/GC-MS. The reaction mixture was filtered and washed with H_2O and Et_2O . The organic phase was separated and dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on silica gel.

The reuse of MFI zeolite-supported catalyst **2**

In the recycling experiment, the reaction was performed by using a mixture of aryl halide (1.0 mmol), phenylboronic acid (134 mg, 1.1 mmol), K_3PO_4 (424 mg, 2.0 mmol), TBAB (129 mg, 0.4 mmol) and catalyst **2** (13.5 mg, 0.3 mol%) in H_2O (3.0 mL) at 65 °C for 0.5 h. After completion of the reaction, the catalyst in the reaction mixture was separated from the solution by a centrifuge. The solution was worked up as described above. The separated catalyst was successively reused for the next reaction without any pretreatment.

Conclusions

In conclusion, hierarchical MFI zeolite was used as a support for immobilization of $Pd(OAc)_2$ -ionic liquid matrix. In this work, ionic liquid fragments were anchored on the mesopore walls of the zeolite. An ionic liquid phase with $Pd(OAc)_2$ was then immobilized into the covalently grafted ionic liquid framework. The resulting catalyst exhibited excellent catalytic activity and high stability for Suzuki coupling reactions in water. This catalyst was recycled four times without a significant loss in the catalytic activity. Hierarchical MFI zeolite was proven to be a promising support for the supported ionic liquid catalysis.

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