

Pd(OAc)₂ Immobilized on Fe₃O₄ as Magnetically Separable Heterogeneous Catalyst for Suzuki Reaction in Water

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Suzuki reaction is one of the most valuable for the construction of aromatic carbon-carbon bond.¹ Palladium catalysts are known to possess high activity for the coupling reaction.² However, the homogeneous catalysis encounters with difficulty of separating the catalyst from the product and reusing the expensive catalyst. Moreover, the homogeneous Pd catalysts tend to lose their catalytic activity due to Pd metal aggregation and precipitation. These problems are of environmental and economic concern in large scale-synthesis. Heterogenation of the existing homogeneous Pd catalysts could be an attractive solution to this problem because the heterogeneous catalysts can be easily separated from the reaction mixture.³

Ionic liquids have attracted much attention as environmentally acceptable alternatives to volatile organic solvents for catalytic reactions.⁴ Palladium catalyzed reactions could be performed in ionic liquids in order to recycle the homogeneous catalysts. However, this reaction system requires a large amount of expensive ionic liquid. It would be desirable to reduce the amount of ionic liquid phase from an economic and toxicological viewpoint. Recently, ionic liquids have been introduced as support media combined with solid support materials.⁵ However, the leaching of catalysts is responsible for severe drawbacks in some cases. The search for efficient and recyclable ionic liquid support catalysts is still a major challenge.

Most of immobilized catalysts are separated by filtration or centrifugation. In contrast, Fe₃O₄-supported catalysts can be separated from the reaction system by an external permanent magnet.⁶ In this context, we envisaged that Fe₃O₄-supported ionic liquid (IL) would be served as an attractive support material. Our interest in this area has prompted us to explore the immobilization of Pd(OAc)₂ on the surface of Fe₃O₄-IL. Herein, we report magnetically recoverable Pd(OAc)₂@Fe₃O₄-IL catalyst for the Suzuki coupling reaction in water.

A silanized ionic liquid was immobilized on the surface of nano-Fe₃O₄ particles **1** in order to enhance the interaction between the surface and free ionic liquid. Modified Fe₃O₄ **2** was prepared by treatment of Fe₃O₄ with 1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride ([tmim][Cl])⁷ in refluxing toluene. The loading capacity of Fe₃O₄ was confirmed to be 0.67 mequiv/g of [tmim][Cl] *via* both elemental analysis and weight gain. Pd(OAc)₂@Fe₃O₄ **3** was obtained by immersing the modified Fe₃O₄ **2** in CH₂Cl₂ solution of Pd(OAc)₂ and [bmim][PF₆], followed by evaporating CH₂Cl₂ from the mixture and washing with diethyl ether. Pd(OAc)₂ was captured in the thin ionic liquid layers through this simple process. The weight composition

ratio of **3** is 1.0 Fe₃O₄ 2 : 0.07 [bmim][PF₆] : 0.04 Pd(OAc)₂, in which the molar ratio of [bmim][PF₆] to Pd(OAc)₂ is 1.45 : 1. Inductively coupled plasma (ICP) analysis indicated that the Pd content is 0.15 mmol/g for **3**. TEM image of Pd(OAc)₂@Fe₃O₄-IL **3** shows that Pd particles are not formed during the formation of **3**, which indicates that Pd(OAc)₂ was homogeneously embedded in ionic liquid layers on the surface of Fe₃O₄-IL support. The Pd(OAc)₂ in the ionic liquid layers would act like a homogeneous species. This system thus may possess the advantages of both homogeneous and heterogeneous catalysts to some extent.

We investigated Suzuki coupling reaction of aryl bromide with phenylboronic acid in the presence of 0.5 mol% of **3** (Table 1). The initial investigation started with the coupling between bromobenzene and phenylboronic acid in pure water. Biphenyl was obtained in 90% conversion at 85 °C after 6 h (entry 1). A phase transfer agent, tetrabutylammonium bromide (TBAB), was added to enhance the reactivity of the reaction. The reaction

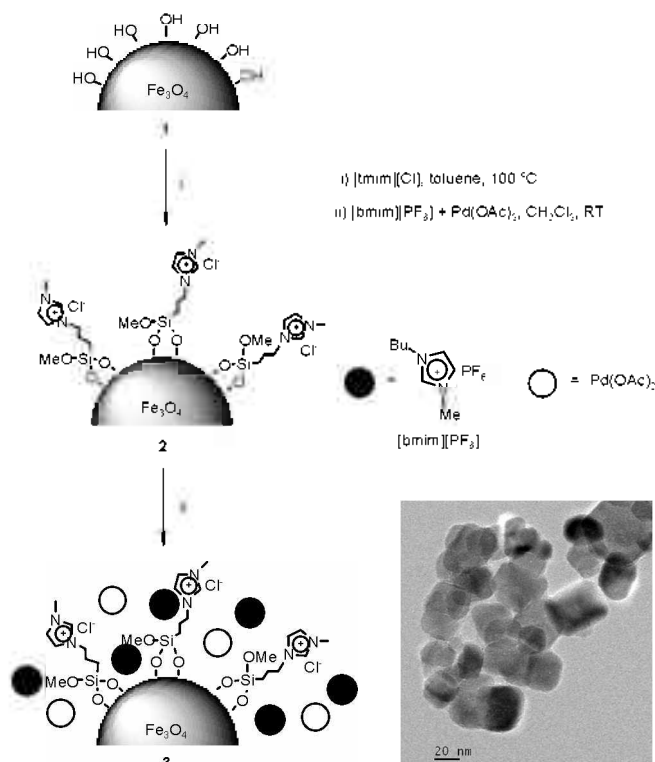
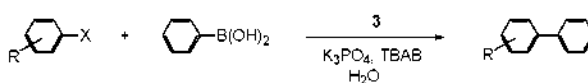



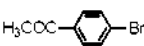
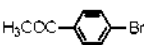
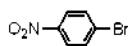
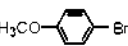

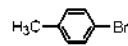



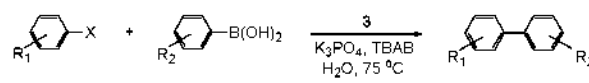
Figure 1. Synthetic scheme and TEM image of **3**.


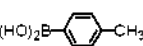
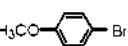
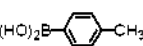
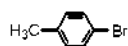
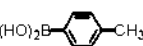

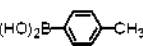
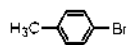
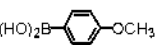

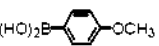
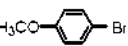
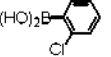

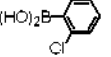
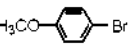
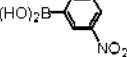
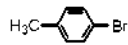
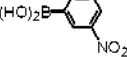


Table 1. Suzuki coupling of aryl bromide with phenylboronic acid in water^a


entry	aryl bromide	time (h)	T (°C)	yield ^b (%)
1 ^c		6	85	91
2		0.8	75	97
3		0.5	65	98
4		0.5	65	97
5		2.0	40	91
6		2.5	40	92
7		1.0	75	96
8		1.0	75	94
9		1.0	75	95
10		2.0	90	90

^aMolar ratio: aryl bromide (1.0 equiv), phenylboronic acid (1.2 equiv), **3** (0.5 mol%), TBAB (0.5 equiv), and K₃PO₄·H₂O (2.0 equiv). ^bIsolated yields. ^cReaction in the absence of TBAB.

proceeded to completion at 75 °C within 1.0 h and all of the starting material was converted to product (entry 2). It seems that the addition of TBAB increases the substrate solubility in water. This catalytic system was then applied to the coupling reactions of various aryl bromides with phenylboronic acid. Activated aryl bromides such as 1-bromo-4-nitrobenzene and 4-bromoacetophenone were rapidly coupled in quantitative yields (entries 3 and 4). These reactions proceeded well even at low temperature of 40 °C (entries 5 and 6). High reactivity for deactivated 4-bromoanisole, 2-bromoanisole, and 4-bromotoluene was still observed (entries 7-9). Furthermore, sterically hindered 2-bromo-1,3-dimethylbenzene also reacted with phenylboronic acid at 90 °C to give the coupled product in satisfactory yield (entry 10). The high efficiency of catalyst **3** is probably attributed to the fact which well-dispersed Pd(OAc)₂ in the ionic liquid phase is more accessible to the reactants. The catalytic system was further extended to the coupling reaction of aryl bromides with different arylboronic acids (Table 2). Deactivated aryl bro-

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


entry	aryl bromide	arylboronic acid	time (h)	yield ^b (%)
1			0.8	95
2			0.8	93
3			1.0	95
4			1.0	92
5			1.0	91
6			1.0	95
7			0.8	91
8			1.0	90
9			0.7	94
10			0.7	92
11 ^c			3.0	87

^aMolar ratio: aryl bromide (1.0 equiv), arylboronic acid (1.2 equiv), **3** (0.5 mol%), TBAB (0.5 equiv), and K₃PO₄·H₂O (2.0 equiv). ^bIsolated yields. ^cReaction temp. was 90 °C.

mides were efficiently coupled with electron-rich 4-methylphenylboronic acid and 4-methoxyphenylboronic acid in high yields (entries 1-6). Catalyst **3** also exhibited excellent activity in the coupling of the aryl bromides with electron-deficient arylboronic acids such as 2-chlorophenylboronic acid and 3-nitrophenylboronic acid (entries 7-10). Nearly complete conversions were achieved for the reactions within short reaction times. Coupling of sterically hindered 2-bromo-1,3-dimethylbenzene with 4-methoxyphenylboronic acid afforded the product in satisfactory yield, although somewhat higher temperature and longer time were required (entry 11). We believe that this catalyst can be applicable to a wide range of arylboronic acids in all cases.

We turned our attention to the reusability of our catalyst **3**. Separation and reuse of catalysts is an important aspect in the heterogeneous reaction.⁸ An attractive advantage of our catalyst

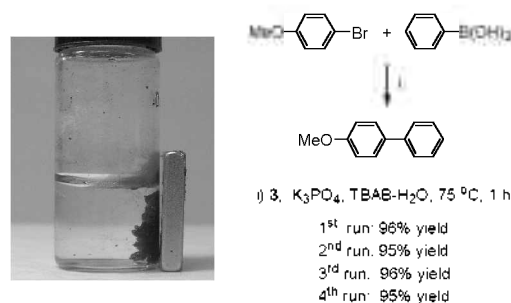


Figure 2. Magnetic separation and recycling of catalysts **3** in Suzuki coupling of 4-bromoanisole with phenylboronic acid.

is its easy separation by using external magnets. The loss of the catalyst can be neglected in the process of separation. The recycling of **3** was investigated by the coupling of 4-bromoanisole with phenylboronic acid in water (Figure 2). The catalyst after each run was recovered by simple decantation, and then was reused in the next run. The catalytic activity of **3** was significantly unchanged during four cycles. This excellent reusability and high stability of **3** would be explained by strong binding of Pd(OAc)₂ to the modified Fe₃O₄. The presence of the supported ionic liquid phase contributes significantly to the direct supporting of Pd(OAc)₂ on the surface. In addition to the high activity, the successful recycling of this catalytic system allows for a more economic and environmentally friendly process.

In summary, the Pd(OAc)₂@Fe₃O₄-IL showed excellent catalytic activity and high stability for the Suzuki coupling reaction in water. This heterogeneous catalyst was reused without a significant loss in the catalytic activity. Moreover, recovery of the catalyst by an external permanent magnet was facile and efficient. Further applications of Fe₃O₄-ionic liquid support are now in progress.

Experimental Section

Surface modification of nano-Fe₃O₄. To a solution of 1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride (0.28 g, 1.0 mmol) in toluene was added Fe₃O₄ (Aldrich, 1.0 g). The mixture was stirred at 100 °C for 10 h. After cooling, the nano-Fe₃O₄ was magnetically separated from reaction mixture. Modified Fe₃O₄ **2** was washed with CH₂Cl₂ several times and dried at 60 °C under vacuum. Weight gain showed that 0.67 mmol of 1-(3-trimethoxy silylpropyl)-3-methylimidazolium chloride was anchored on 1.0 g of **2**.

Immobilization of Pd(OAc)₂ onto modified nano-Fe₃O₄. To a solution of Pd(OAc)₂ (40 mg, 0.18 mmol) and 1-butyl-3-methylimidazolium hexafluorophosphate (70 mg, 0.25 mmol) in CH₂Cl₂ (1 mL) modified Fe₃O₄ **2** (1.0 g) was added. The mixture was sonicated for 15 min at room temperature, and then CH₂Cl₂ was slowly removed under reduced pressure. The re-

sulting powder was washed with diethyl ether and dried under vacuum at 60 °C to give Pd(OAc)₂@Fe₃O₄-IL **3** (1.11 g). The Pd content of 0.15 mmol/g was measured by inductively coupled plasma (ICP) analysis.

General procedure for the Suzuki reaction. Aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), K₃PO₄·H₂O (460 mg, 2.0 mmol), TBAB (161 mg, 0.5 mmol), dodecane (20 mg, internal standard) and catalyst **3** (33 mg, 0.5 mol%) were mixed in H₂O (2.5 mL). The mixture was stirred at 75 °C in an air atmosphere. After magnetic separation of the catalyst, the organic material was twice extracted with diethyl ether. The organic phase was dried over MgSO₄ and the solvent was evaporated under reduced pressure. The crude was analysed by GC/GC-MS. The product was purified by short-column chromatography on silica gel. In the recycling experiment, the separated catalyst was successively reused for the next reaction without any pretreatment.

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