



Biogenous iron oxide-immobilized palladium catalyst for the solvent-free Suzuki–Miyaura coupling reaction

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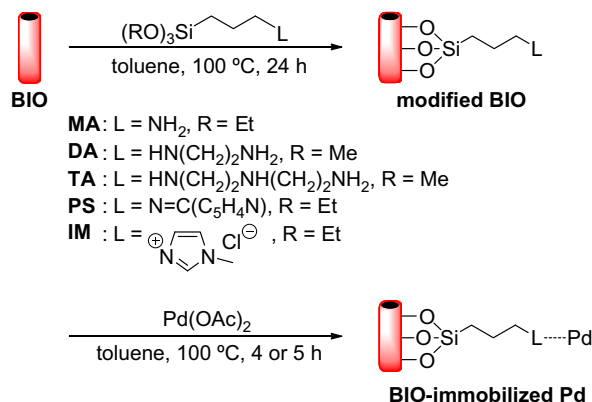
ABSTRACT

Iron oxide produced by iron-oxidizing bacteria, *Leptothrix ochracea*, (biogenous iron oxide: BIO) was used as a support for immobilized palladium catalysts with organic cross-linkers. Palladium immobilized on BIO bearing imidazolium chloride delivered the desired biaryl products in sufficient yields in the Suzuki–Miyaura coupling reactions under solvent-free conditions and could be reused several times without significant loss of catalytic activity. It is shown that BIO can be exploited as a useful support for immobilization of palladium and the BIO-immobilized palladium catalyst effectively promotes the solvent-free Suzuki–Miyaura coupling reactions.

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Introduction

Microbially-produced iron oxide, particularly produced by iron-oxidizing bacteria, *Leptothrix ochracea*, is referred to as biogenous iron oxide (BIO) and has a unique amorphous and porous hollow microtube structure that cannot be constructed artificially.¹ The fascinating structure of BIO was elucidated by Takada and his co-workers,¹ and its application to new functional materials is the subject of active investigations. We have recently reported the preparation of lipase immobilized on BIO through organic cross-linkers and its use in the kinetic resolution of secondary alcohols.² The BIO-immobilized lipase showed high catalytic activity probably because of the specific shape, surface, and nanostructure of BIO suitable for the dispersion of each enzyme molecule on the surface of BIO. The structure of the organic cross-linker was also found to have a critical role for the enzymatic activity. These results encouraged us to investigate the utilization of BIO as a support for transition metal catalysts such as palladium catalysts.^{3,4} In particular, the Suzuki–Miyaura coupling reaction, one of the well-known palladium-catalyzed reactions, has been widely used for practical syntheses of various biphenyl-type organic compounds.⁵ Although most reactions are performed using homogeneous catalytic systems, many immobilized palladium catalysts on a variety of supports such as polymer, carbon, mesoporous silica, zeolite, or metal oxides have been studied to improve the cat-



Scheme 1. Schematic representation of the preparation of BIO-immobilized Pd catalysts.

alytic activity and recyclability.⁶ In this study, we report the development of a BIO-immobilized palladium catalyst for the Suzuki–Miyaura coupling reactions. The unique structure of BIO was found to enhance the catalytic activity in the coupling reactions, either in water solvent or under solvent-free conditions.

Results and discussion


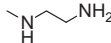
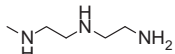
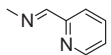
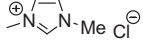
We attempted to modify the surface of BIO with substituted trialkoxysilanes bearing various functional groups at their termini,

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Table 1

Analytical data of modified and BIO-immobilized Pd and results of the Suzuki–Miyaura coupling reactions with BIO-immobilized Pd under various reaction conditions

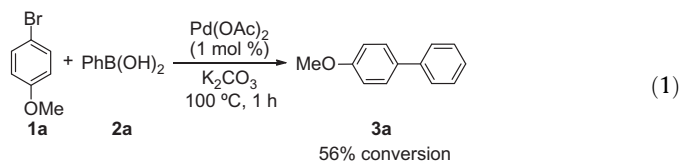
<div><div><div><div><div><div></div><div>MeO</div></div><div><div></div><div></div></div><div><div></div><div>Br</div></div></div></div><div>1a</div></div><div><div><div><div></div><div></div></div><div><div></div><div></div></div><div><div></div><div>B(OH)₂</div></div></div></div><div>2a</div></div> <div><div>BIO-immobilized Pd</div><div>$\xrightarrow{\text{K}_2\text{CO}_3, 50\text{ }^\circ\text{C}, 16\text{ h}}$</div></div> <div><div><div><div></div><div>MeO</div></div><div><div></div><div></div></div><div><div></div><div></div></div></div></div> <div>3a</div>								
Entry	L	Modified BIO		BIO-immobilized Pd		Conversion to 3a (%) ^c		
			Coverage ^a mmol/g (wt %)		Pd content ^b mmol/g (wt %)	Reaction conditions		
						DMF ^d	H ₂ O with TBAB ^e	No solvent ^f
1		BIO-MA	1.48 (12.76)	BIO-MA-Pd	0.62 (6.6)	34	88	87
2		BIO-DA	1.39 (17.43)	BIO-DA-Pd	0.64 (6.8)	40	91	88
3		BIO-TA	0.97 (16.62)	BIO-TA-Pd	0.57 (6.1)	39	65	84
4		BIO-PS	0.77 (13.44)	BIO-PS-Pd	0.48 (5.1)	26	34	89
5		BIO-IM	1.58 (29.68)	BIO-IM-Pd	0.89 (9.4)	55	92	90

^a Determined by elemental analysis.^b Determined by ICP-OES analysis.^c Reactions were performed with 0.30 mmol of 4-bromoanisole (**1a**), 0.33 mmol of phenylboronic acid (**2a**), and 0.60 mmol of K₂CO₃ with 5 mg of BIO-immobilized Pd under the indicated conditions at 50 °C for 16 h. Conversions were determined by analysis of ¹H NMR spectra.^d DMF (1 mL) was added to the mixture of BIO-immobilized Pd, **1a**, **2a**, and K₂CO₃ before stirring in an argon atmosphere.^e H₂O (1 mL) was added to the mixture of BIO-immobilized Pd, **1a**, **2a**, K₂CO₃, and 0.15 mmol of TBAB before stirring in air.^f BIO-immobilized Pd, **2a**, and K₂CO₃ were mixed until homogeneous before addition of **1a** and the mixture was heated in air.

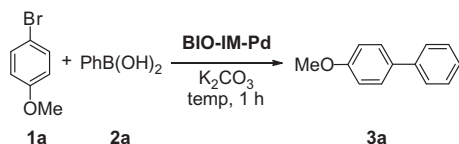
which are capable of coordinating palladium for the attachment of palladium on BIO (Scheme 1). For L groups of trialkoxysilanes, we chose nitrogen-containing functional groups such as monoamine (**MA**), diamine (**DA**), triamine (**TA**), and pyridinyl Schiff base (**PS**). Imidazolium chloride (**IM**), which is a precursor of N-heterocyclic carbene that is well-known as a powerful ligand for metal catalysts,⁷ was also employed. The general preparation procedure for modified BIO and BIO-immobilized Pd is shown in Scheme 1. Commercial (**MA**, **DA**, **TA**) or prepared (**PS**, **IM**) trialkoxysilanes and BIO were mixed in dry toluene at 100 °C for 24 h in an argon atmosphere. Subsequently, the modified BIO was treated with Pd(OAc)₂ in dry toluene at 100 °C for 4–5 h. BIO-immobilized Pd was obtained after washing and drying under vacuum. Analytical data of the modified BIO and the BIO-immobilized Pd as well as the catalytic activity of the palladium catalysts in the Suzuki–Miyaura coupling reactions are listed in Table 1. The coverage of organic cross-linkers on BIO is 0.77–1.58 mmol/g (12.76–29.68 wt %), as determined by elemental analysis, and the palladium content of BIO-immobilized Pd catalysts is in a range of 0.48–0.89 mmol/g (5.1–9.4 wt %), as determined by ICP-OES analysis.

The catalytic activity of BIO-immobilized Pd was investigated in the Suzuki–Miyaura coupling reaction of 4-bromoanisole (**1a**) and phenylboronic acid (**2a**) as representative substrates and K₂CO₃ as a base. The reactions were performed in the presence of 5 mg of BIO-immobilized Pd in *N,N*-dimethylformamide (DMF) at 50 °C for 16 h. Incidentally, the reaction did not proceed in the presence of 5 mg of unmodified BIO. As shown in Table 1, conversions to the desired 4-methoxybiphenyl (**3a**) were from 26 to 55%, and **BIO-IM-Pd** exhibited the best catalytic activity (55% conv.) among them. Instead of DMF, water was used as a solvent in combination with tetra-*n*-butylammonium bromide (TBAB) for the reaction.⁸ All palladium catalysts gave improved conversions in the reactions in water as compared to the reactions in DMF. Among them, **BIO-IM-Pd** also yielded the best conversion (92% conv.). At this point, it was assumed that the reaction would actually proceed in liquid 4-bromoanisole (**1a**), and not in the water layer. Thus, the reactions of **1a** and **2a** in the presence of BIO-immobilized Pd and K₂CO₃ were performed without solvent at 50 °C for 16 h.⁹ When **BIO-**

MA-Pd, **BIO-DA-Pd**, and **BIO-IM-Pd** were used, conversions to **3a** were comparable to those obtained in the reactions in water. However, **BIO-TA-Pd** and **BIO-PS-Pd** showed their best catalytic activities in the reaction without solvent (84% and 89% conv., respectively). The investigation revealed that **BIO-IM-Pd** gave better overall results involving coverage of organic cross-linkers, Pd content as well as conversions obtained in the Suzuki–Miyaura coupling reactions under three reaction conditions. When **1a** and **2a** were allowed to react with Pd(OAc)₂ and K₂CO₃ as a reference reaction under solvent-free conditions, the product **3a** was obtained with only 56% conversion (Eq. 1). In addition, addition of 1.6 mol % 1-butyl-3-methylimidazolium chloride to the reaction with palladium acetate yielded **3a** in lower conversion (67% conv.). Accordingly, it is unambiguous that the obtained higher reactivity of our catalyst arises from BIO as a support for the immobilized palladium catalyst.



We further investigated the reaction condition to optimize the solvent-free Suzuki–Miyaura coupling reactions of **1a** and **2a** with **BIO-IM-Pd** (Table 2). Various inorganic bases other than K₂CO₃ and triethylamine that are used as a representative organic base were tested in the reaction with the catalyst (1 mol % Pd) at 100 °C for 1 h in air. K₂CO₃ was found to be the best choice to give the highest conversion to the product **3a** (Table 2, entries 1 and 7–13). The reaction with K₂CO₃ at 120 °C gave 90% conversion to **3a** (entry 3). As the reaction temperature decreased, the conversions to **3a** diminished (82% conv. at 80 °C, entry 4, and 63% conv. at 50 °C, entry 5). The reaction can be sufficiently facilitated with 0.1 mol % of the palladium catalyst at 100 °C to give the product **3a** in 84% yield (entry 6). Silica is often used as a support for palladium-immobilized catalysts in the Suzuki–Miyaura coupling reactions.^{6,10} We prepared silica gel-immobilized Pd (**silica gel-IM-Pd**)

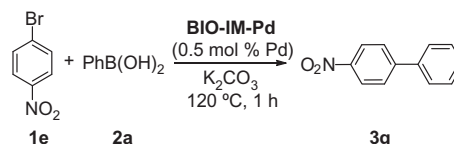
Table 2Screening of reaction conditions of the solvent-free Suzuki–Miyaura coupling reaction^a

Entry	Base	Pd loading (mol %)	Temp (°C)	Conv. ^b (%)	Yield ^c (%)
1	K ₂ CO ₃	1.0	100	90	90
2 ^d	K ₂ CO ₃	1.0	100	53	—
3	K ₂ CO ₃	1.0	120	90	—
4	K ₂ CO ₃	1.0	80	82	—
5	K ₂ CO ₃	1.0	50	63	—
6	K ₂ CO ₃	0.1	100	86	84
7	Na ₂ CO ₃	1.0	100	45	45
8	Cs ₂ CO ₃	1.0	100	74	74
9	K ₃ PO ₄	1.0	100	87	87
10	KOt-Bu	1.0	100	16	—
11	KF	1.0	100	55	56
12	KOH	1.0	100	60	60
13	NEt ₃	1.0	100	5	—

^a The reaction was performed with 0.50 mmol of **1a**, 0.55 mmol of **2a**, and 1.00 mmol of base.^b Determined by analysis of ¹H NMR spectra.^c Isolated yield after purification by silica gel column chromatography with hexane/EtOAc = 50:1.^d **Silica gel-IM-Pd**, which was prepared from commercially available silica gel (BW-127ZH, Fuji Silysia Chemical Ltd., Japan), was used.

similar to **BIO-IM-Pd** according to our preparation procedure and tested it in the reaction with 1 mol % Pd loading at 100 °C for 1 h under solvent-free conditions. As a result, **silica gel-IM-Pd** gave lower conversion as compared to **BIO-IM-Pd** (53% conv., entry 2, vs 90% conv., entry 1), indicating that the catalytic activity was much improved by immobilization on BIO.

The coupling reactions of various aryl halides and arylboronic acids were performed under solvent-free conditions (Table 3).¹¹ The reactions of bromobenzene (**1b**) and arylboronic acids bearing electron-donating and electron-withdrawing groups (**2b–e**) furnished the desired products **3b–d** in 77–91% yields (entries 1–4). The reaction of **1b** and 4-(trifluoromethyl)phenylboronic acid (**2f**), which has a low reactivity due to its electron-withdrawing *p*-CF₃ group, was facilitated by 3 mol % Pd catalyst and a longer reaction time to give the product **3e** in good yield (84% yield, entry 5). The coupling between non-substituted **1b** and **2a** delivered the desired product **3f** in 85% yield with 0.5 mol % catalyst at 120 °C for 4 h (entry 6). The reaction of 4-methyl- and 4-fluoro-substituted aryl bromides (**1c** and **1d**) and **2a** afforded **3b** in 84% yield and

Table 4Recycling test of **BIO-IM-Pd** in the reaction of 4-bromonitrobenzene and phenylboronic acid

Run number	1st	2nd	3rd	4th	5th
Conv. ^a (%)	97	98	98	94	94

^a Determined by analysis of ¹H NMR spectra.

3d in 84% yield, respectively (entries 7 and 8). Interestingly, the reaction between 4-bromonitrobenzene (mp 125 °C) (**1e**) and **2a** (mp 217 °C) is a solid-state reaction; however, it provided the desired product **3g** in high yield (95% yield, entry 9). Among the reports on Suzuki–Miyaura coupling reactions without solvent,^{12,13} the solid-state reactions are few.¹⁴ Thus, it is notable that **BIO-IM-Pd** is an effective immobilized palladium catalyst for the solvent-free Suzuki–Miyaura coupling reactions while the reaction was not applicable to the corresponding aryl chlorides such as chlorobenzene and 4-chloroanisole.

Recyclability of **BIO-IM-Pd** was examined in the reaction of **1e** and **2a** in the presence of 0.5 mol % of **BIO-IM-Pd** and K₂CO₃ at 120 °C for 1 h. After the extraction of the coupling product **3g** with ethyl acetate, the **BIO-IM-Pd** was purified by centrifugation and reused in the next reaction with freshly added **1e**, **2a**, and K₂CO₃. This procedure was repeated four times until the 5th run. As shown in Table 4, it was found that the reactivity of the catalyst was maintained over five runs without significant loss of its reactivity. A similar recyclability was also confirmed by using a liquid substrate such as 4-bromoanisole.

To obtain further information on **BIO-IM-Pd**, scanning electron microscopy (SEM) was performed. SEM images of unmodified BIO, **BIO-IM**, and **BIO-IM-Pd** are shown in Figure 1. No significant change of the surface structure was observed on **BIO-IM** in the course of surface modification ((a) and (b)). In the case of **BIO-IM-Pd**, evenly dispersed nanosized particles were detected on the slightly deformed surface of **BIO-IM** (c), although the surface deformation is seen. Average particle size of these particles is 13.2 nm, which was determined by the analysis of SEM images of **BIO-IM-Pd** (the size distribution histogram is in Supplementary data). It is known that palladium nanoparticles¹⁵ or palladium clusters¹⁶ have high catalytic activity. Hence, the observation indicates that the reactivity of our immobilized palladium catalyst is ascribed to palladium nanoparticles that are attached and

Table 3Solvent-free Suzuki–Miyaura coupling reactions of aryl halides and arylboronic acids^a

ArX + Ar'B(OH) ₂		BIO-IM-Pd		Ar-Ar'					
1 + 2		K ₂ CO ₃ , temp, time		3					
Entry	ArX	Ar'	Pd loading (mol %)	Temp (°C)	Time (h)	Product	Conv. ^b (%)	Yield ^c (%)	
1	Bromobenzene	1b 4-Methylphenyl	2b 1.0	120	4	3b	83	77	
2	Bromobenzene	1b 4-Methoxyphenyl	2c 0.5	100	1	3a	91	91	
3	Bromobenzene	1b 3-Fluorophenyl	2d 0.5	120	1	3c	88	83	
4	Bromobenzene	1b 4-Fluorophenyl	2e 0.5	120	1	3d	93	82	
5	Bromobenzene	1b 4-(Trifluoromethyl)phenyl	2f 3.0	120	16	3e	94	84	
6	Bromobenzene	1b Phenyl	2a 0.5	120	4	3f	90	85	
7	4-Bromotoluene	1c Phenyl	2a 0.5	120	1	3b	92	84	
8	4-Bromofluorobenzene	1d Phenyl	2a 0.5	100	1	3d	95	84	
9	4-Bromonitrobenzene	1e Phenyl	2a 0.5	120	1	3g	98	95	

^a Reactions were performed with 0.50 mmol of ArX, 0.55 mmol of Ar'B(OH)₂, and 1.00 mmol of K₂CO₃ with **BIO-IM-Pd** in air.^b Determined by analysis of ¹H NMR spectra.^c Isolated yield after purification by silica gel column chromatography.

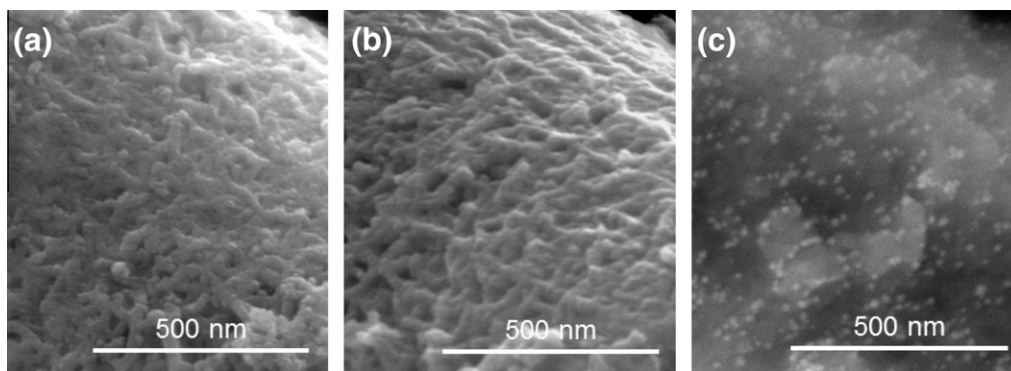


Figure 1. SEM images of (a) BIO, (b) BIO-IM, and (c) BIO-IM-Pd.

dispersed well on the surface of modified BIO, and these palladium nanoparticles promote the Suzuki–Miyaura coupling reactions. Detailed analysis of the catalyst and its role in the solvent-free Suzuki–Miyaura coupling reactions will be further investigated.

In conclusion, we have prepared new types of BIO-immobilized palladium catalysts and successfully applied them to the Suzuki–Miyaura coupling reactions. Combination of the porous nanostructure of BIO and choice of suitable organic cross-linker notably enhanced the catalytic activity to promote the reaction even in a non-solvent system as well as in a solid-state system. The catalyst could be reused at least five times and was useful. Developing the functional utility of naturally produced and ubiquitous materials such as BIO will be an urgent subject for environmentally benign synthesis.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.11.044.

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