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A nanostructured skeleton catalyst: Suzuki-coupling with a reusable and sustainable nanoporous metallic glass Pd-catalyst†

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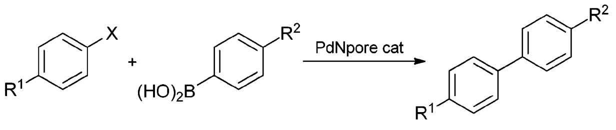
Nanoporous metallic glass Pd, which was fabricated by dealloying of a glassy metallic alloy $Pd_{30}Ni_{50}P_{20}$, exhibited a remarkable catalytic activity for the Suzuki-coupling reaction between iodoarenes and arylboronic acids under mild conditions. Moreover, the catalyst can be reused several times without a significant loss of catalytic activity.

Suzuki-coupling catalyzed by palladium is one of the most important organic transformations in recent years.[1] A palladium molecular catalyst, such as **A**, is used in general, which consists of a single palladium atom (Fig. 1). Needless to say, bulk palladium metal **D** does not exhibit catalytic activity to the coupling reaction. Recently, small palladium particles **B**, consisting of gathering of palladium atoms, have been used as a catalyst, but a drawback of this catalyst is that it undergoes quite easily agglomeration under the reaction conditions, leading to deactivation of the catalyst.[2,3] We wish to report for the first time that palladium nanoporous materials catalyst **C**, which is a nanostructured skeleton catalyst, exhibits high catalytic activity to the Suzuki-coupling and it can be used several times without a significant loss of catalytic activity (Scheme 1).



Scheme 1 PdNpore-catalyzed Suzuki coupling.

Recently, the fabrication method of nanoporous palladium from metallic glassy ribbons was reported by Inoue, Chen and co-workers.[4,5] In comparison with crystalline alloys, multicomponent metallic glasses are monolithic in phase with a homogeneous composition and structure down to the subnanoscale. This property is effective for formation of nanoporosity uniformly upon dealloying, because the nanoporosity is produced by a self-assembly process through surface diffusion, not by the simple excavation of one phase from a preseparated multiphase system. A requisite nanoporous palladium catalyst for the present reaction was also fabricated under the standard conditions[4] by electrochemical dealloying of metallic glass $Pd_{30}Ni_{50}P_{20}$ ribbon with about 15 μm thickness for 2 h in 1 mol L^{-1} H_2SO_4 using a classical three-electrode setup. Then, the resulting nanoporous Pd ribbon was cut into small pieces (approximately 5 mm × 1 mm). A SEM image showed the resulting nanoporous structures of a dealloyed metal (Fig. 2a), and the nanopore size was around 30–60 nm. EDX analysis indicated that the composition of the dealloyed metal was $Pd_{67}Ni_{23}P_{10}$ (Fig. 2c).

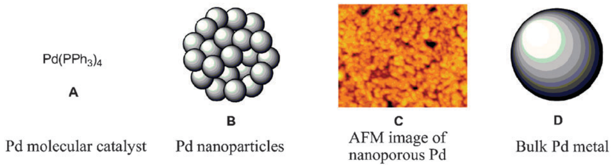


Fig. 1 From a Pd molecular catalyst **A** to a nanostructured materials catalyst **C**.

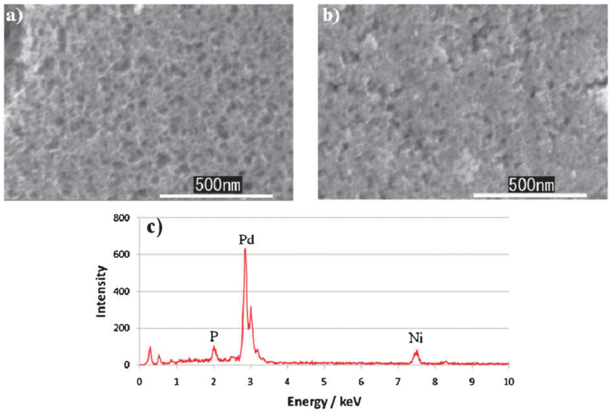


Fig. 2 Scanning electron microscopy (SEM) images of nanoporous metallic glass Pd (a) before reaction, (b) after 4 times run of the Suzuki-coupling reaction of iodobenzene with *p*-tolylboronic acid, (c) Energy Dispersive X-ray spectroscopy (EDX) analysis of nanoporous metallic glass Pd.

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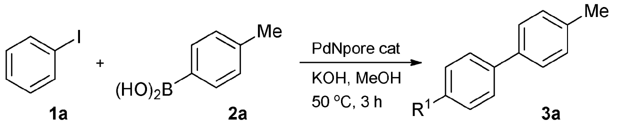
Table 1 Reusability of nanoporous metallic glass Pd for Suzuki-coupling[a]



Entry	PdNpore	%Yield of **3a**[b]
1	Fresh	99
2	Reuse 1	94
3	Reuse 2	92
4	Reuse 3	95

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.75 mmol), KOH (2.5 mmol), PdNpore (2 mol%), MeOH (2 mL). [b] Isolated yield.

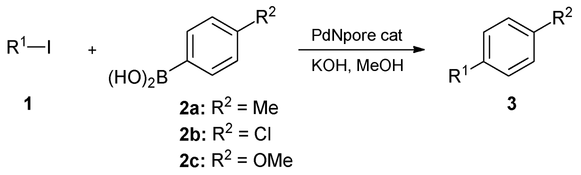
We initially investigated the reaction of iodobenzene (**1a**) with *p*-tolylboronic acid (**2a**) catalyzed by nanoporous Pd. The reaction of **1a** with **2a** using KOH as a base in the presence of 2 mol% nanoporous Pd in MeOH at 50 °C for 3 h gave the corresponding biphenyl product **3a** in quantitative yield (run 1 in Table 1). On the other hand, no coupling products were obtained in the presence of un-dealloyed (non-porous) metallic glass $Pd_{30}Ni_{50}P_{20}$ or in the absence of nanoporous Pd. These results indicate that the nanoporous structure plays a crucial role in catalyzing the reaction.

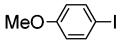
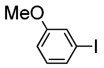
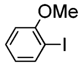
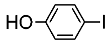
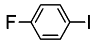
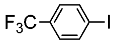
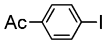
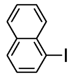
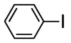
It is well known that agglomeration of palladium decreases the catalytic activity, hence appropriate stabilizer or supporter is necessary to prevent deactivation by agglomeration.[2,3] In contrast, the nanoporous Pd exhibited excellent catalytic activity under mild reaction conditions without any supporter, ligand, or stabilizer. Palladium black has been also reported as an unsupported catalyst for Suzuki coupling between arylboronic acids and aryl iodides. However, the reaction was conducted with nearly one-half equivalent of catalyst probably due to the poor catalytic activity.[6] Recovery of ordinary heterogeneous catalysts often requires cumbersome treatment. In contrast, the recovery process in the current catalytic system is simple. Since the size of the catalyst is relatively large, the catalyst and the product can be separated easily by just removal of the liquid moiety by a pipette. The recovered catalyst was washed with MeOH several times and it was reused without further treatment. Indeed, the product **3a** could be obtained in excellent yield every time when the reactions were performed 4 times (Table 1). A SEM image of the catalyst after 4 times run indicated the nanoporous structure was maintained well (Fig. 2b).

We next examined the reaction to know whether a dissolved Pd species in solvents participates in the current molecular transformation or not. Leaching of the palladium was not detected during or after reaction of **1a** with **2a** by inductivity coupled plasma (ICP-AES) analysis (<0.0005%).[7] We also checked the leaching by conducting the reaction with the supernatant. The reaction of **1a** with **2a** was carried out for 30 min under the standard conditions, then a half amount of solution was picked up. ^{1}H NMR analysis of the supernatant indicated that **3a** was produced in 3% yield at this time. The supernatant was stirred in the absence of the catalyst for 3 h; the chemical yield of **3a** at this moment was 24%. On the other hand, stirring of the residual reaction mixture having the catalyst for 3 h gave **3a** in 93% yield. These results clearly indicated that dissolved Pd species existed and catalyzed the reaction but its activity was much lower than that of the solid state of the catalyst. The leaching of Pd from the solid state catalytic system in the Suzuki-coupling has been investigated well and a lot of efforts have been paid to reduce the leaching amount of Pd.[8] In the current catalytic system, however, we believe that the leaching amount is quite small.

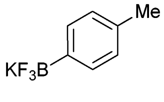
The Suzuki-coupling reactions using various reactants were examined (Table 2). The reaction of 4-iodoanisole (**1b**) with **2a** proceeded smoothly at 50 °C for 4 h and the corresponding coupling product **3b** was obtained in 95% yield. The reaction speed was influenced significantly by the electronic effect of the substituents on the arylboronic acid. For example, the reaction of **1b** with 4-chlorophenylboronic acid (**2b**) was sluggish and it required 12 hours. In contrast, the reaction with 4-methoxyphenylboronic acid (**2c**) completed in 1 hour (entries 1–3). The reaction proceeded smoothly even with sterically hindered 2-iodoanisole (**1d**) (entry 5). The reactions of aryl iodides

Table 2 Scope and limitations of the Suzuki-coupling reaction catalyzed by nanoporous metallic glass Pd[a]

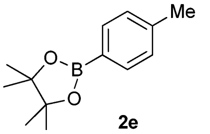


Entry	1	R^1-I	2	Condition	Product % yield[b]
1	**1b**		**2a**	50 °C, 4 h	**3b**, 95
2	**1b**		**2b**	50 °C, 12 h	**3c**, 95
3	**1b**		**2c**	50 °C, 1 h	**3d**, 83
4	**1c**		**2a**	50 °C, 5 h	**3e**, 95
5	**1d**		**2a**	50 °C, 6 h	**3f**, 79
6	**1e**		**2a**	80 °C, 12 h	**3g**, 89
7	**1f**		**2a**	50 °C, 3 h	**3h**, 99
8	**1g**		**2a**	50 °C, 0.5 h	**3i**, 99
9	**1h**		**2a**	50 °C, 2 h	**3j**, 95
10	**1i**		**2a**	50 °C, 3 h	**3k**, 99
11	**1a**		**2d**	50 °C, 4 h[c]	**3a**, 87
12	**1a**		**2e**	80 °C, 3 h	**3a**, 78
13	**1a**		**2f**	80 °C, 4 h[d]	**3a**, 95

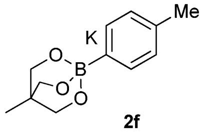
[a] Reaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), KOH (2.5 mmol), PdNpore (2 mol%), MeOH (2 mL). [b] Isolated yield. [c] The reaction was conducted in a mixture of MeOH (1.2 mL) and H_2O (0.6 mL). [d] The reaction was conducted in the absence of KOH.



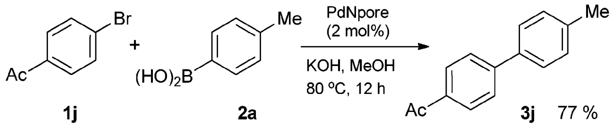
2d



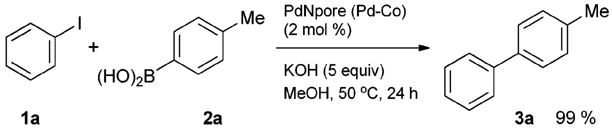
2e



2f



Scheme 2 PdNpore-catalyzed Suzuki coupling with arylbromide.



Scheme 3 PdNpore (Pd–Co)-catalyzed Suzuki coupling.

possessing electron-withdrawing groups (entries 7–9) proceeded faster than those having electron-donating groups (entries 1 and 6). Besides boronic acids, other arylboron compounds, **2d–f**, were suitable reactants in this catalytic system (entries 11–13).

The nanoporous palladium catalyzed the coupling reaction not only with aryl iodide but also with aryl bromide. For example, the reaction of **1j** and **2a** proceeded smoothly and the corresponding product **3j** was obtained in 77% yield (Scheme 2).

Recently, Hakamada and Mabuchi have reported the fabrication method of nanoporous palladium from a Pd–Co alloy.[9] We wondered if it exhibited a catalytic activity like the material derived from Pd–Ni–P metallic glass. According to the literature, we conducted selective corrosion of cobalt from a $Pd_{20}Co_{80}$ alloy by electrochemical way to produce a nanoporous palladium. Then, we used it as a catalyst for Suzuki coupling between **1a** and **2a**. To our delight, the reaction proceeded and the product **3a** was obtained in nearly quantitative yield (Scheme 3).

To know the level of Pd leaching in this reaction, we investigated the catalytic activity of the supernatant as we did with the catalyst from the metallic glass. The coupling reaction between **1a** and **2a** with a PdNpore (Pd–Co) catalyst was carried out for 2.5 h in the reaction vessel-1. At this time, product **3a** was formed in 14% yield. Then, a half amount of supernatant was transferred to another reaction vessel-2 and it was stirred for 21.5 h without catalyst. However, no progress of the reaction was observed at all. On the other hand, the remaining half amount of supernatant with the catalyst in the vessel-1 gave **3a** in 97% yield after the same 21.5 h. Furthermore, we confirmed that the reaction mixture in the vessel-2 gave **3a** quantitatively by use of the recovered catalyst from the vessel-1.[7] These results clearly indicated that the reaction catalyzed by nanoporous palladium fabricated from Pd–Co is a heterogeneous process.

We are now in a position to carry out the Suzuki coupling with the nanoporous palladium catalysts fabricated from Pd–Ni–P metallic glass and Pd–Co alloy. It is worthy to mention that the catalyst does not need any supports unlike supported Pd nanoparticles such as Pd/C. Moreover, it does not require any ligands or stabilizers in spite of its metallic agglomerate morphology. The catalyst can be easily recovered by a simple separation process and reused several times without significant loss of catalytic activity. Furthermore, the leaching amount of Pd was lower than the detection limits of ICP-AES. Further studies to elucidate details of the current reaction are in progress.

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