

## Supporting Information

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

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### 1. General

NMR spectra were measured at 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C by JEOL JNM-AL 400 spectrometer. Chemical shifts of <sup>1</sup>H NMR were expressed in parts per million downfield from tetramethylsilane with reference to tetramethylsilane ( $\delta = 0.00$ ) in CDCl<sub>3</sub>. Chemical shifts of <sup>13</sup>C NMR were expressed in parts per million downfield from CDCl<sub>3</sub> as an internal standard ( $\delta = 77.0$ ) in CDCl<sub>3</sub>. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (Kieselgel 60 F254, 0.2 mm) were used. The products were purified by flash column chromatography on silica gel 60 N (KANTO, 40-50 mm). SEM observation was carried out using HITACHI FE-SEM S4300 operated at an accelerating voltage of 10 kV. EDX analysis was carried out using EDAX Genesis with HITACHI FE-SEM S4300 operated at an accelerating voltage of 20 kV. ICP-AES analysis was performed with Shimadzu ICPS-7510.

### 2. Reagent and solvent

Aryl iodides, aryl bromides, and KOH were purchased and used as received. Arylboronic acids were synthesized by literature procedure<sup>1</sup> or purchased and used as received. MeOH was purchased from Kanto Chemical co.,inc. for HPLC grade and used as received without further purification.

### 3. Fabrication of nanoporous metallic glass Pd

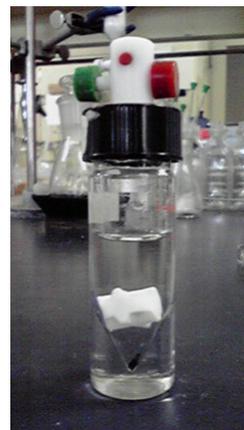
Mother alloy Pd<sub>30</sub>Ni<sub>50</sub>P<sub>20</sub> was prepared by arc melting a mixture of pure Ni and Pd metals and pre-alloyed Pd-P ingots in an argon atmosphere. The rapidly solidified ribbon sample with a thickness of about 15 μm was prepared by the single-roller melt spinning technique.<sup>2</sup>

A classical three-electrode setup (Iviumstat electrochemical analyzer, Ivium Technology) was employed to dealloy the Pd<sub>30</sub>Ni<sub>50</sub>P<sub>20</sub> glassy ribbons using Ag/AgCl electrode as the reference. A section of Pd<sub>30</sub>Ni<sub>50</sub>P<sub>20</sub> ribbon (length = abt. 5 cm, width = abt. 1 mm, thickness = abt. 15 μm) was placed as the working electrode and a pure platinum sheet positioned parallel to the Pd<sub>30</sub>Ni<sub>50</sub>P<sub>20</sub> sample was used as the counter electrode. The electrolyte is 500 mL of 1 mol/L H<sub>2</sub>SO<sub>4</sub> which was prepared from conc.H<sub>2</sub>SO<sub>4</sub> and deionized water and was used immediately. The optimized condition for dealloying the Pd<sub>30</sub>Ni<sub>50</sub>P<sub>20</sub> metallic glasses is 0.8 V for 2 h at room temperature. The dealloyed samples were taken out of the solution and rinsed with deionized water and acetone for several times, then dried (see: right picture).



### 4. General procedure of Suzuki-coupling

To a solution of KOH (140 mg, 2.5 mmol) in MeOH (2 mL) were added **1a** (101 mg, 0.50 mmol) and **2a** (103 mg, 0.75 mmol) at room temperature. The resulting homogeneous solution was added V-shaped vial reactor containing nanoporous Pd (1.0 mg, 2 mol%), and the reaction mixture was stirred for 3 h at 50 °C with bulky round-shaped magnetic stirring bar to avoid the contact between the catalyst and stirring bar (see: right figures). The liquid moiety was transferred to the separation funnel by a pipette and was extracted with ethyl acetate three times. The combined extracts were evaporated to leave the crude product, which was purified by silica gel column chromatography with hexane to give **3a** (83.4 mg) in 99% yield.



The recovered catalyst was washed with MeOH several times, and it was reused without further purification.

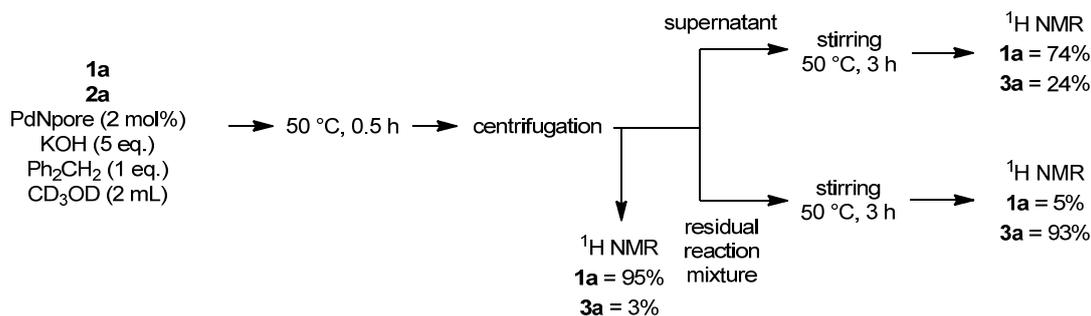
Spectral data of the following compounds are consistent with previously published literature values: **3a**,<sup>3</sup> **3b**,<sup>4</sup> **3c**,<sup>4</sup> **3d**,<sup>5</sup> **3e**,<sup>6</sup> **3f**,<sup>7</sup> **3g**,<sup>8</sup> **3h**,<sup>3</sup> **3i**,<sup>9</sup> **3j**,<sup>10</sup> **3k**.<sup>11</sup>

## 5. ICP analysis

Two sets of the reaction of **1a** with **2a** were carried out for 1 and 3 h at 50 °C by the general Suzuki-coupling procedure respectively. Then, a half amount of the clear solution (1 mL) was picked up and the solvent was evaporated under reduced pressure. The residue was dissolved in aqua regia (1 mL), then it was diluted with distilled water up to 100 mL. The precipitate was filtered off, and the filtrate was analyzed by ICP-AES.

## 6. Leaching test for nanoporous metallic glass Pd

To a solution of KOH (136 mg, 2.5 mmol) in methanol- $d_4$  (2 mL) were added **1a** (104 mg, 0.50 mmol), **2a** (104 mg, 0.75 mmol), diphenylmethane (83.6 mg, 0.50 mmol, internal standard) at room temperature. The resulting homogeneous solution was added to the V-shaped vial reactor containing nanoporous Pd (0.9 mg, 2 mol%), and the reaction mixture was stirred for 0.5 h at 50 °C. After centrifugation of the mixture, 50  $\mu$ L of the supernatant was picked up for checking the chemical yield of **3a** with  $^1\text{H}$  NMR. Then, 1 mL of the supernatant was transferred to another vial reactor, and it was stirred for 3 h at 50 °C in the absence of the catalyst. The chemical yield of **3a** was checked again by picking up 50  $\mu$ L of the resulting solution. On the other hand, the residual reaction mixture having the catalyst continued to stir for 3 h in parallel, then the chemical yield of **3a** in the mixture was observed by  $^1\text{H}$  NMR (Scheme S1).



Scheme S1. Experimental flow of leaching test

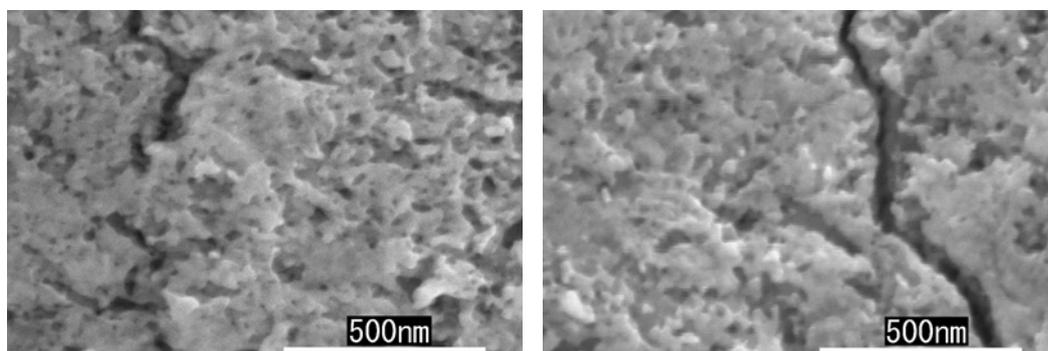
## 7. Fabrication of nanoporous Pd fabricated from Pd<sub>20</sub>Co<sub>80</sub><sup>12</sup>

Mother alloy Pd<sub>20</sub>Co<sub>80</sub> was prepared by arc melting a mixture of pure Co and Pd metals in an argon atmosphere. Then, the alloy ingot sealed in the silica tube under vacuum was heated at 900 °C for 24 h for homogenization. After homogenization, the alloy was water-quenched. The surface oxide scale generated by water quenching was removed mechanically. Then, the alloy was rolled to less than 100  $\mu$ m thickness.

A classical three-electrode setup (Iviumstat electrochemical analyzer, Ivium Technology) was employed to dealloy the Pd<sub>20</sub>Co<sub>80</sub> ribbons using saturated calomel electrode as the reference. A section of Pd<sub>20</sub>Co<sub>80</sub> ribbon (length = abt. 2 cm, width = abt. 3 mm, thickness = abt. 100  $\mu$ m) was placed as the working electrode and a pure platinum sheet positioned parallel to the Pd<sub>20</sub>Co<sub>80</sub> sample was used as the counter electrode. The electrolyte is 500 mL of 0.1 mol/L H<sub>2</sub>SO<sub>4</sub>. The condition for dealloying the Pd<sub>20</sub>Co<sub>80</sub> alloy is 0.5 V for 12 h at room temperature. The dealloyed

samples were taken out of the solution and rinsed with deionized water and acetone for several times, then dried.

## 8. SEM of nanoporous Pd fabricated from Pd<sub>20</sub>Co<sub>80</sub> before/after reaction

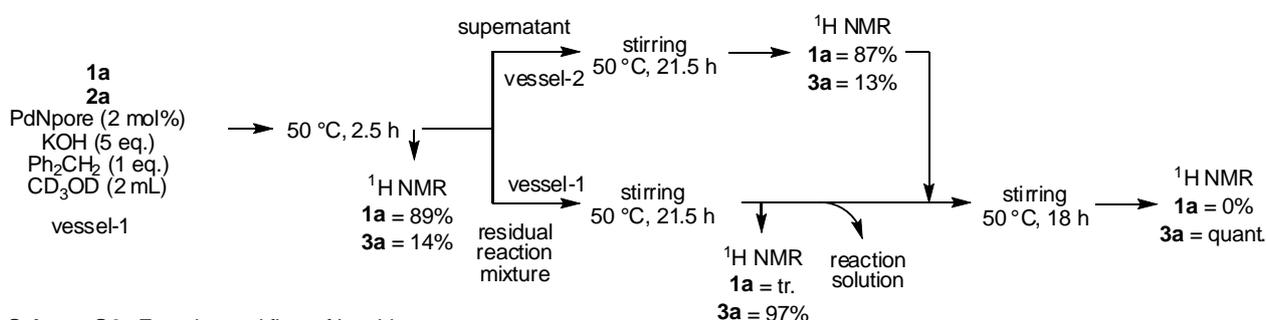


(a) Before reaction

(b) After reaction

## 9. Leaching test for nanoporous Pd fabricated from Pd<sub>20</sub>Co<sub>80</sub>

To a solution of KOH (128 mg, 2.5 mmol) in methanol-d<sub>4</sub> (2 mL) were added **1a** (103 mg, 0.50 mmol), **2a** (102 mg, 0.75 mmol), diphenylmethane (82.3 mg, 0.50 mmol, internal standard) at room temperature. The resulting homogeneous solution was added to the V-shaped vial reactor (vessel-1) containing nanoporous Pd (1.1 mg, 2 mol%), and the reaction mixture was stirred for 2.5 h at 50 °C. At this stage, 50 μL of the supernatant was picked up for checking the chemical yield of **3a** with <sup>1</sup>H NMR. Then, 1 mL of the supernatant was transferred to vessel-2, and it was stirred for 21.5 h at 50 °C in the absence of the catalyst. The chemical yield of **3a** was checked again by picking up 50 μL of the resulting solution. On the other hand, the residual reaction mixture in vessel-1 having the catalyst continued to stir for 21.5 h in parallel, then the chemical yield of **3a** in the mixture was observed by <sup>1</sup>H NMR. Furthermore, the reaction mixture in vessel-2 was transferred to vessel-1 after removal of the reaction solution in vessel-1, and it was stirred for 18 h at 50 °C in the presence of the catalyst. The chemical yield of **3a** was checked again by picking up 50 μL of the resulting solution. (Scheme S2).



**Scheme S2.** Experimental flow of leaching test

## 10. References

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