Advanced Synthesis & Catalysis

Accepted Article

Title: Development of a unique heterogeneous palladium catalyst for Suzuki–Miyaura reaction using (hetero)aryl chlorides and chemoselective hydrogenation

Authors: Tomohiro Ichikawa, Moeko Netsu, Masahiro Mizuno, Tomoteru Mizusaki, Yukio Takagi, Yoshinari Sawama, Yasunari Monguchi, and Hironao Sajiki

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201700156

Link to VoR: http://dx.doi.org/10.1002/adsc.201700156

10.1002/adsc.201700156

FULL PAPER

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Development of a unique heterogeneous palladium catalyst for Suzuki–Miyaura reaction using (hetero)aryl chlorides and chemoselective hydrogenation

Tomohiro Ichikawa,[a] Moeko Netsu,[a] Masahiro Mizuno,[a] Tomoteru Mizusaki,[b] Yukio Takagi,[b] Yoshinari Sawama,[a] Yasunari Monguchi[a]* and Hironao Sajiki[a]*

[a] Laboratory of Organic Chemistry, Gifu Pharmaceutical University, 1-25-4 Daigaku-nishi, Gifu 501-1196, Japan. Phone/Fax: (+81)-58-230-8109; e-mails: monguchi@gifu-pu.ac.jp and sajiki@gifu-pu.ac.jp

[b] Chemical Catalysts R & D Department, Catalyst Development Center, N.E. Chemcat Corporation, 25-3 Kojindaira, Bando, Ibaraki 306-0608, Japan

Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract. A unique heterogeneous palladium catalyst (7% Pd/WA30) supported on an anion exchange resin, which contains *N*,*N*-dimethylaminoalkyl functionalities on the polymer backbone, was developed. 7% Pd/WA30 could smoothly catalyze Suzuki–Miyaura reaction of even less reactive heteroaryl chlorides and heteroaryl boronic acids to afford various (hetero)biaryls due to the electron-donating effect of the *tert*-amines on WA30 to Pd species. It was also applicable as a chemoselective hydrogenation catalyst, showing inactivity for the hydorogenolysis of *tert*-butyldimethylsilyl (TBS) ethers, alkyl benzyl ethers, and benzyl alcohols. The *tert*-amines on WA30 acted as moderate catalyst poisons for Pd, resulting in chemoselective hydrogenation. 7% Pd/WA30 was reused for at least five times without any loss of the hydrogenation catalytic activity.

Keywords: Chemoselectivity; Heterogeneous catalysis; Hydrogenation; Palladium; Suzuki–Miyaura reaction

Introduction

Development of heterogeneous Pd catalysts has been investigated for a long time in termes of process chemistry, due to their notable advantages over homogeneous Pd catalysts, such as recoverability, reusability, and less residual metal property, which are directly linked to the reduction of environmental and economic burdens.[1] The Pd-catalyzed Suzuki-Miyaura reaction between aryl halides and arylboronic acids has been widely applied for the synthesis of biaryls, which are often present in many biologically active compounds.[2,3] The addition of phosphine or amine ligands favors the smooth reaction progress, although they are often expensive and toxic. As opposed to the number of ligand-free Suzuki-Miyaura reactions of aryl iodides or bromides using heterogeneous catalysts,[4,5] only a few heterogeneous catalysts could be applied to the ligand-free protocols of less reactive chloroarenes[6,7] despite their versatility and low cost. We have already developed a heterogeneous Pd catalyst immobilized on a synthetic adsorbent, DIAION HP20 [(HP20, Mitsubishi Chemical Corporation), Pd/HP20],[8] which is a polystyrene-divinylbenzene polymer without special functionalities on the polymer backbone. Pd/HP20 indicates the high catalytic activity for the ligand-free Suzuki-Miyaura reaction of bromoarenes in aqueous alcohols, although aryl chlorides are still inappropriate as substrates.[5b,5d] Pd/HP20 also catalyzes the hydrogenation of a wide variety of reducible functionalities.[5b] However, specific functionalities that coexist with multiple reducible functional groups in a single molecule could not be selectively reduced, because of the high catalyst activity.

Chemoselective hydrogenation is an important topic in synthetic chemistry because of its contribution to the development of new synthetic pathways.[9,10] To date, various heterogeneous Pd catalysts have been developed for the chemoselective hydrogenation of alkenes, alkynes, carbonyl, and nitro functionalities in the presence of protecting groups,[11–18] such as benzyl ethers,[16a,16b,16p,18b–e,18h–j] benyl esters,[16b,18c–e,18h–j] and *N*-benzyloxycarbonyls (Cbz),[16a,18c,18e,18h–j] hydrogenation of alkenes in the presence of carbonyl[16c–e,18c,18e,18h–i] or nitro groups,[16a,18e,18h–j] and semi-hydrogenation of alkynes to the corresponding alkenes.[16f–o,18g] Furthermore, heterogeneous Pd-catalyzed chemoselective hydrogenolysis methods for the deprotection have also been reported; e.g., the deprotection of benzyl ethers in the presence of trisubstituted olefines,[17] and the removal of *N*-Cbz and *O*-benzyl protections to the corresponding amines, phenols, and carboxylic acids without hydrogenation of carbonyl functionality.[18f]

We have established various Pd/C-catalyzed chemoselective hydrogenation systems using NH_4OAc,[18a] ethylenediamine,[18b] and diphenylsulfide[18c] as catalytic poisons. Moreover, we developed catalyst support-dependent chemoselective hydrogenation methods using Pd on

This article is protected by copyright. All rights reserved.

Accepted Manuscript

ceramic,[18d,18e] monolithic ion exchange resin,[18f] fibroin as a protein,[18g,18h] molecular sieves 3Å,[18e,18h–j] boron nitride,[18e,18h–k] and the chelate resins, DIAION CR11 or CR20 bearing a diiminoacetate or polyamine moiety, respectively.[18e,18l] The catalyst activity of such catalysts basically depends on the ingredients of supports, which can interact or coordinate with Pd species, and the chemoselectivity could be achieved by the appropriate reduction of the inherent activity of Pd species.[18h]

A commercially available anion exchange resin, DIAION WA30 (WA30, Mitsubishi Chemical Corporation),[19,20] bearing *N*,*N*-dimethylaminoalkyl groups on the polystyrene-divinylbenzene backbone was a preferable target as a catalyst support, because the *tert*-amino functionalities of WA30 would act as moderate ligands to Pd metal. 7% Pd/WA30 was prepared by the adsorption of palladium diacetate [$Pd(OAc)_2$] to the colorless WA30 in ethyl acetate and its subsequent reduction using hydrazine.[21–23] It is noteworthy that it could effectively catalyze the Suzuki-Miyaura reaction of chloroarenes. We have reported the preliminary results focusing on the coupling between non-heterocyclic aromatic chlorides and boronic acids.[21] Although heterogeneous catalysts for Suzuki–Miyaura reaction of chloroarenes with a ligand function on their support display the greatest catalyst activity, such intramolecular ligands may act as a catalyst poison in hydrogenation reactions.[7] Therefore, we expected that the effective catalyst for the Suzuki–Miyaura reaction may be applicable to the chemoselective hydrogenation as a less active catalyst.

In this paper, we describe the 7% Pd/WA30-catalyzed Suzuki-Miyaura reaction using aryl and heteroaryl chlorides and its new application for chemoselective hydrogenation.

Results and Discussion

The properties of 7% Pd/WA30 were analyzed by X-ray photoelectron spectroscopy (XPS), scanning transmission electron microscope (STEM),[21] X-ray diffraction (XRD) spectroscopy, and electron probe microanalysis (EPMA). 7% Pd/WA30 consisted of both Pd(II) and Pd(0) species even after reduction with hydorazine, as shown in the XPS image (see the Supporting information and also reference 21). The particle size of Pd species was estimated to be approximately 3–20 nm by means of the STEM image (see the Supporting information and also reference 21).The XRD analysis indicated that the existence of crystalline palladium in the 7% Pd/WA30 (Figure 1), and the particle size of Pd species was evaluated to be ca. 4 nm, which were virtually conformed to that estimated from STEM image.[24] Furthermore, the EPMA indicated that the Pd species were securely fastened to the surface layer of WA30 (Figure 2).

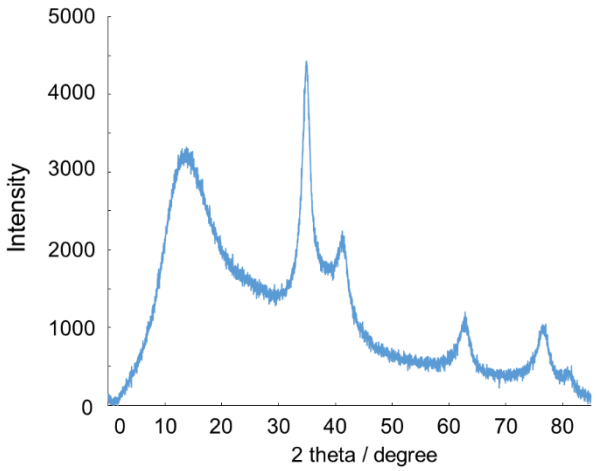


Fig. 1 XRD spectrum of 7% Pd/WA30

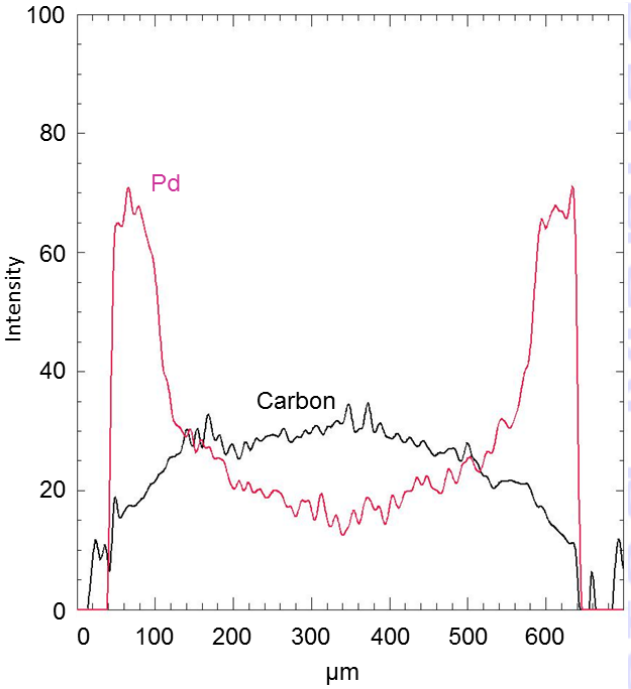


Fig. 2 EPMA spectrum of 7% Pd/WA30

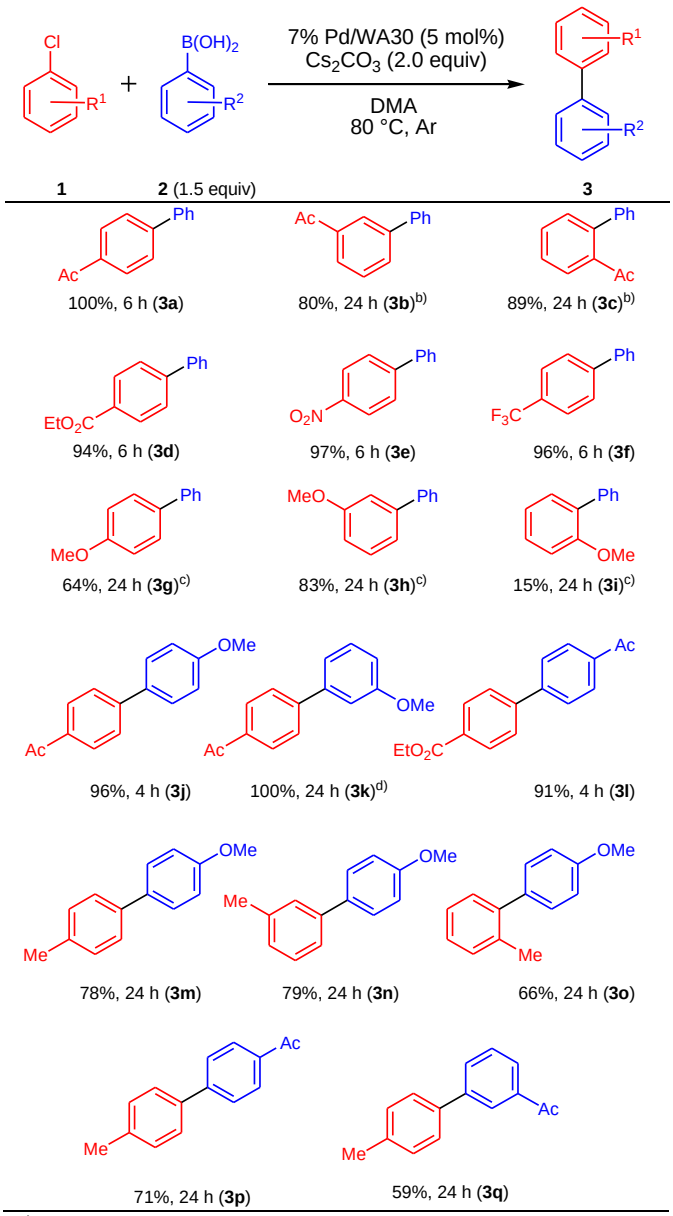
As we preliminarily reported in the communication, 7% Pd/WA30 could catalyze the Suzuki–Miyaura coupling reaction between various aryl chlorides and arylboronic acids in the presence of Cs_2CO_3 in *N*,*N*-dimethylacetamide (DMA) at 80 °C (Table 1).[21] Phenylation of chloroarenes bearing an electron-withdrawing group such as Ac (**3a–c**), CO_2Et (**3d**), NO_2 (**3e**), and CF_3 (**3f**) on the aromatic ring smoothly occurred to afford the corresponding biaryls in high to excellent yields. Although it is difficult to react chloroanisoles (**3g** and **3h**) bearing an electron-rich aromatic ring with phenylboronic acid, the yield was improved by increasing the amounts of the catalyst, phenylboronic acid, and Cs_2CO_3. However, the yield of 2-methoxybiphenyl did not improve in spite of using increased amounts of such reagents, probably because of the electronic and steric properties of 2-

This article is protected by copyright. All rights reserved.

Accepted Manuscript

chloroanisole. Substituted phenylboronic acids were also used for the cross-coupling reaction (**3i–q**).[25] Even unfavorable combinations of the coupling reagents, such as electron-rich chlorotoluenes and electron-poor acetylphenylboronic acids (**3p** and **3q**), afforded the desired biaryls in good to high yields.

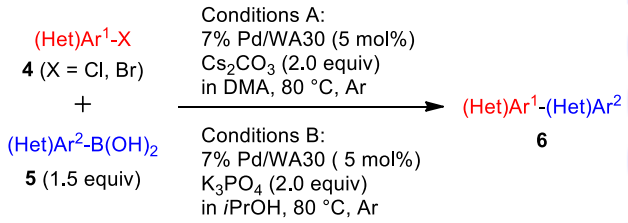
Table 1. Coupling of chloroarenes and boronic acids[a]



[a] Reactions were carried out on a 0.25 mmol scale in 1 mL of DMA. [b] The reaction was performed using 2 equiv of phenylboronic acid. [c] The reaction was carried out using 10 mol% of 7% Pd/WA30, 3 equiv of Cs_2CO_3, and 3 equiv of phenylboronic acid. [d] The reaction was performed using 2 equiv of 3-methoxyphenylboronic acid.

Heterobiaryls are of particular interest as fundamental scaffolds of a variety of medicines, natural products, functional materials, etc. Although the Suzuki–Miyaura reaction has been one of the most effective synthetic methods of non-heterobiaryl units, only a few successful couplings of heteroaryl chlorides, especially under ligand-free heterogeneous conditions, have been reported in the literature.[6g–h] Heteroaryl halides and heteroaryl boronic acids are generally less reactive than non-heteroaromatic halides and boronic acids owing to the potential coordination of heteroatoms with Pd species. Thus, we precisely investigated the catalytic activity of 7% Pd/WA30 for the Suzuki–Miyaura coupling reaction for the preparation of heterobiaryls. A coupling of 4- or 3-chloropyridine and non-heteroaryl boronic acids afforded the corresponding 4- or 3-arylated pyridine in high yields (**6a–d**) in the presence of Cs_2CO_3 in DMA at 80 °C (conditions A). A relatively low yield (30%) of 2-pheylpyridine (**6e**) was obtained from 2-chloropyridine under conditions A despite using increased amounts of 7% Pd/WA30, phenylboronic acid, and Cs_2CO_3. However, the yield of **6e** increased to 56% yield when K_3PO_4 was used as a base and *i*PrOH as a solvent (conditions B). The coupling of 2-chloropyridine and non-heteroaryl boronic acids was also feasible (**6e–g**). The yield of 2-arylated pyridines increased to good to high yields using more reactive 2-bromopyridines as the substrate. The arylation of 2-chloroquinoline smoothly proceeded to yield the corresponding heterobiaryls in excellent yields regardless of the electron density of the benzene ring of aryl boronic acids (**6h** and **6i**): the sterically hindered 2-methoxyphenylboronic acid was also applicable to this arylation (**6j**). Reactions of non-heteroaryl chlorides and heteroaryl boronic acids were successfully performed under conditions A (**6k** and **6l**), although the corresponding heteroaryl boronic acids were unstable under conditions B and the yields greatly decreased because of the decomposition of the boronic acids before the cross-coupling reaction. It was remarkable that 7% Pd/WA30 could also catalyze the formation of heterobiaryls (**6m** and **6n**). However, the coupling of 2-chloropyridine with 2-benzofuranylboronic acid was unsuccessful under both conditions A and B (**6o**).

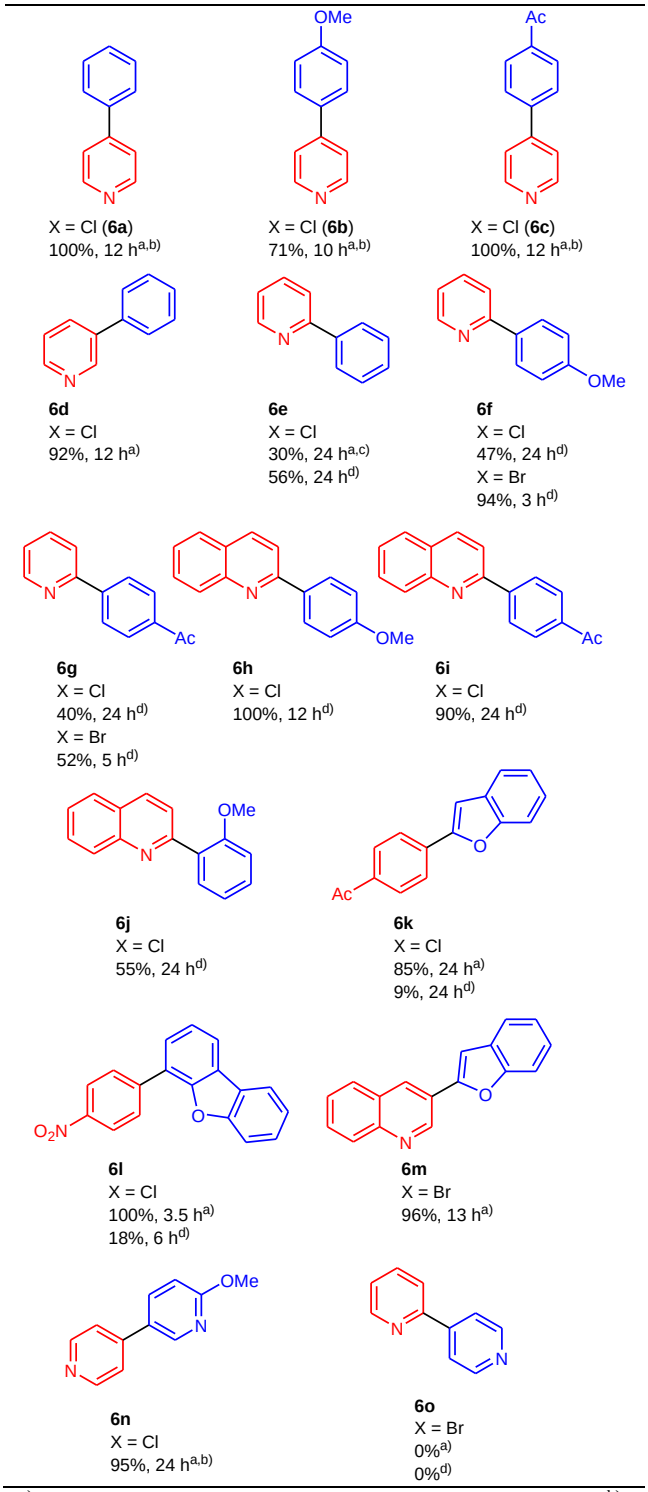
Table 2. Suzuki–Miyaura reaction of (hetero)aryl halide with (hetero)aryl boronic acids[a]



This article is protected by copyright. All rights reserved.

Accepted Manuscript

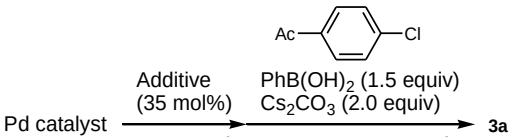
10.1002/adsc.201700156



[a] The reaction was carried out under conditions A. [b] 4-Chloropyridine hydrochloride salt was used as a substrate and 3 equiv of Cs_2CO_3 was used. [c] The reaction was carried out using 10 mol% of 7% Pd/WA30, 3 equiv of Cs_2CO_3, and 3 equiv of phenylboronic acid. [d] The reaction was carried out under conditions B.

We used 10% Pd/HP20 pre-treated with amine derivatives for the Suzuki–Miyaura reaction of 4'-chloroacetophenone and phenylboronic acid to investigate whether the *tert*-aminoalkyl group on WA30 has actually act as a ligand to Pd (Table 3). 10% Pd/HP20 was stirred with tertiary amines, such as Me_2NBn (Entry 3), Et_3N (Entry 5), and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA, Entry 7), without solvents at room temperature for 1 h under an Ar atmosphere for the Pd species on the 10% Pd/HP20 directly to interact with the *tert*-amines.[26] The same pre-treatment experiments using 7% Pd/WA30 were also conducted as the control experiments (Entries 4, 6, 8). 10% Pd/HP20 catalyzed the reaction to provide 4-acetylbiphenyl in 75% yield without pre-treatments by additives, while the use of the pre-treated catalysts for the reaction provided the virtually same results (Entries 3, 5, 7 vs. 1). Similarly, the effect of the pre-treatment of the catalyst with amines was barely observed in the case of 7% Pd/WA30 (Entries 4, 6, 8 vs. 2). It has also been proposed that the single-electron transfer (SET) process is involved in the activation of a carbon-halogen bond as the reaction mechanism.[27–31] We have reported that SET from Pd species to aromatic chlorides caused the activation and cleavage of the C-Cl bond in the presence of amines.[32,33] Since the addition of a radical scavenger (2,2,6,6-tetramethylpiperidine 1-oxyl, TEMPO) never affected the reaction yield (Entry 5), the *tert*-amine functionality on WA30 would not facilitate the SET from Pd to substrates. These results indicate that external amines would neither function as ligands to Pd nor initiate the SET process; we considered that the Pd species accepted an electron pair from *tert*-amino group via an intramolecular coordination as a ligand, rather than an intermolecular Pd-*tert*-amine interaction, in addition to the π-electrons of the polystyrene backbone aromatic ring due to strong coordination. The combination of the two interaction ways would result in the excellent catalytic activity of 7% Pd/WA30.

Table 3. Mechanistic study of *tert*-amino group on WA30



Entry	Catalyst	Additive	Yield (%)[a]
1	10% Pd/HP20	none	75
2[b]	7% Pd/WA30	none	100[c]
3	10% Pd/HP20	Me_2NBn	80
4[b]	7% Pd/WA30	Me_2NBn	100
5	10% Pd/HP20	Et_3N	80
6[d]	7% Pd/WA30	Et_3N	88[e]
7	10% Pd/HP20	TMEDA	70
8[b]	7% Pd/WA30	TMEDA	93
9[b]	7% Pd/WA30	TEMPO	96

[a] The yield was determined by ^1H NMR using 1,4-dioxane as an internal standard. [b] The reaction was completed in 6 h. [c] Isolated yield. [d] The reaction was carried out for 6 h. [e] 8% of starting material was recovered. [f] The coupling reaction between 4'-chloroacetophenone and phenylboronic acid (1.5 equiv) was carried out in the presence of 7% Pd/WA30 (5 mol%), Cs_2CO_3 (2.0 equiv), and 2,2,6,6-tetramethylpiperidine (10 mol%) without pre-treatment of 7% Pd/WA30. TMEDA = *N*,*N*,*N*',*N*'-

Accepted Manuscript

This article is protected by copyright. All rights reserved.

10.1002/adsc.201700156

tetramethylethylenediamine. TEMPO = 2,2,6,6-tetramethylpiperidine 1-oxyl.

In our preliminary report, we proved that 7% Pd/WA30 could be quantitatively recovered by a simple filtration after the Suzuki–Miyaura reaction, and no leached Pd species from 7% Pd/WA30 to the reaction media were detected by inductively coupled plasma-atomic emission spectrometry (ICP-AES).[21] However, the coupling reaction of 4'-chloroacetophenone with phenylboronic acid slightly but surely proceeded in the filtrate obtained after the removal of 7% Pd/WA30 by the filtration without cooling. These results strongly suggest the "release and capture" process of the Pd species from and on the support (WA30). During the reuse test of 7% Pd/WA30, its catalytic activity decreased drastically even in the second reuse of the catalyst. According to the XPS spectra of 7% Pd/WA30 before and after the reaction, the ratio of Pd(0)/Pd(II) increased after the reaction (see the Supporting information). Furthermore, the EPMA spectrum of 7% Pd/WA30 after the reaction indicates that Pd species were uniformly distributed from the surface to the inside of WA30 (Figure 3), although this distribution was obviously deflected to the surface of the WA30 support (Figure 2). Therefore, we have concluded that the decrease of Pd species on the WA30 surface, which directly catalyze the coupling reaction, caused the decrease of the catalytic activity due to the difficult uptake of substrates inside the support, owing to the comparatively small surface area (15 m^2 g^{-1}) and pore volume (1.3 mL g^{-1}) of WA30.[6,20]

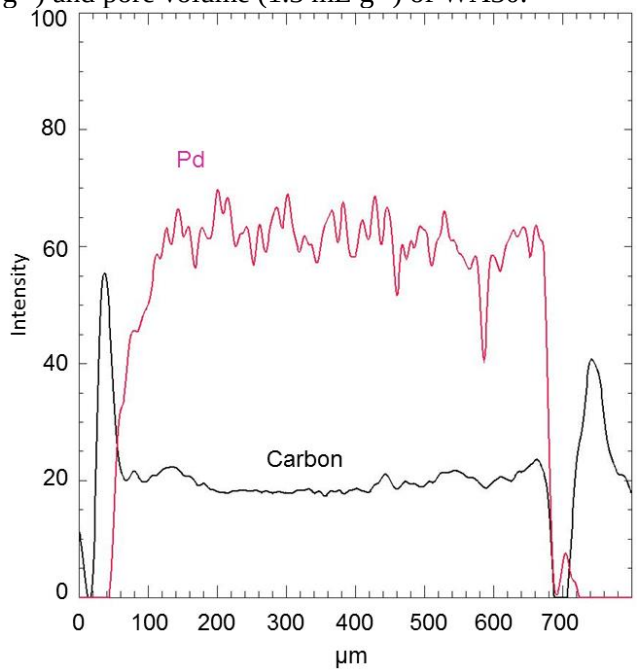
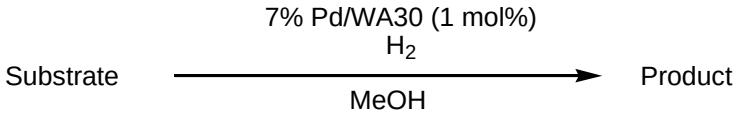


Fig. 3 EPMA spectrum after Suzuki–Miyaura reaction

The catalytic activity of 7% Pd/WA30 for the hydrogenation was evaluated in MeOH using substrates bearing a variety of reducible groups. The hydrogenation of alkynes (Table 4, Entries 1, 9, and 10), azido (Entry 2), alkene (Entries 3, 7, 11, 15, 18, and 23), and nitro (Entries 3 and 4) functionalities smoothly proceeded at room temperature under ordinary hydrogen pressure. Aryl ketones (Entries 5 and 6) and an aldehyde (Entry 7) were reduced at 40 °C to obtain the corresponding benzyl alcohols without any further hydrogenolysis of the benzyl alcohol functionality even after being stirred for 24 h. Benzyl alcohols (Entries 8 and 9) are likewise inert during the 7% Pd/WA30-catalyzed hydrogenation. The *N*-Cbz protecting group of both aliphatic and aromatic amines could be removed (Entries 10–14). The deprotection of aryl benzyl ethers and benzyl esters was easily performed at room temperature (Entries 15–19). It is noteworthy that aliphatic benzyl ethers could be tolerant under the same reaction conditions (Entries 19–21). The selective hydrogenolysis of the benzyl ester of Boc-Ser(Bn)-OBn was achieved without the deprotection of the coexisting aliphatic benzyl ether (Entry 19). Furthermore, epoxide adjacent to aromatic rings easily opened to afford the corresponding benzyl alcohol (Entry 22). *tert*-butyldimethylsilyl (TBS) protecting group could also tolerate under the reaction conditions (Entry 23).

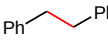
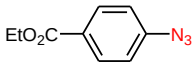
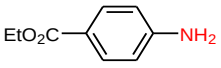
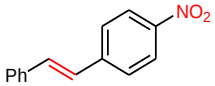
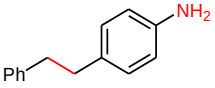
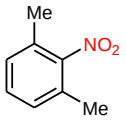
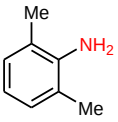
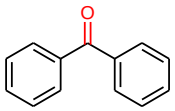
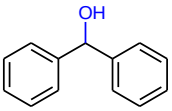
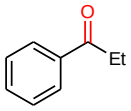
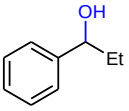
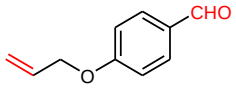
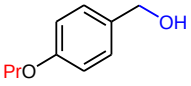
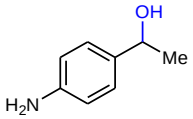
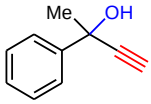
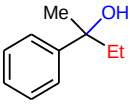
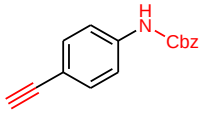
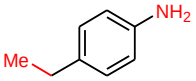
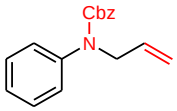
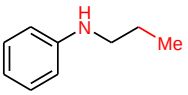
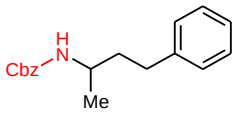
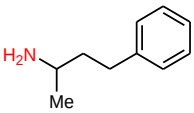
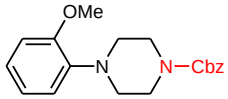
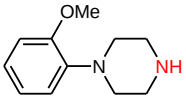
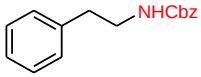
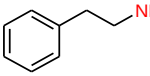
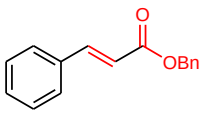
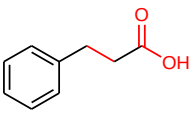
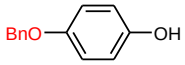
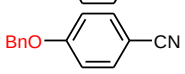
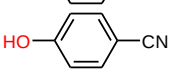
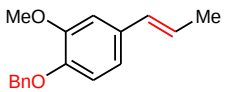
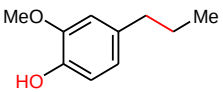
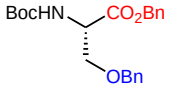
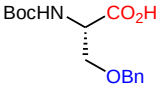
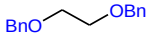
Table 4. 7% Pd/WA30-catalyzed hydrogenation



Accepted Manuscript

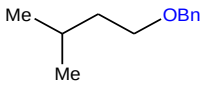
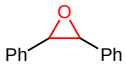
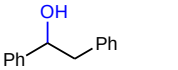
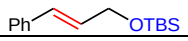
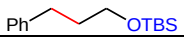
This article is protected by copyright. All rights reserved.

10.1002/adsc.201700156

Entry	Substrate	Temp. (°C)	Time (h)	Product	Ratio[a)] (**SM** : **Pro**)
1		rt	5		0 : 100 (100)
2		rt	18		0 : 100 (100)
3		rt	24		trace : 99 (89)
4		rt	24		0 : 100 (81)
5		40	6		0 : 100 (100)
6		40	24		0 : 100 (100)
7		40	24		0 : 100 (94)
8		rt	24	No Reaction	100 (100) : 0
9		rt	24		0 : 100 (99)
10		40	24		0 : 100 (89)
11		rt	24		0 : 100 (98)
12		rt	7		0 : 100 (100)
13		rt	8		0 : 100 (100)
14		50	24		0 : 100 (76)
15		rt	7		0 : 100 (98)
16		rt	6		0 : 100 (100)
17		rt	6		0 : 100 (94)
18		rt	18		0 : 100 (100)
19		rt	24		0 : 100 (75)
20		rt	24	No Reaction	100 (96) : 0

Accepted Manuscript

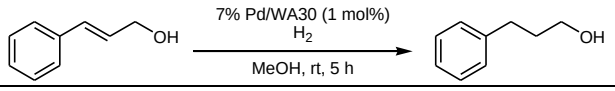
This article is protected by copyright. All rights reserved.

21		rt	24	No Reaction	100 (91) : 0
22		rt	18		0 : 100 (98)
23		rt	24		0 : 100 (98)

[a] Ratio was determined by ^{1}H NMR. Isolated yields are indicated in parentheses.

Next, the reuse of 7% Pd/WA30 under the hydrogenation conditions was examined using cinnamyl alcohol as a substrate (Table 5). The catalyst could be readily recovered and reused for at least five times without any loss of the catalytic activity. Furthermore, the leached Pd species in the filtrate of the reaction mixture were never detected by ICP-AES (detection limit: <1 ppm).

Table 5. Reuse of 7% Pd/WA30



Run	1st	2nd	3rd	4th	5th
Recovered 7% Pd/WA30	97	100	97	97	96
Yield (%)	100	100	100	100	100

Figure 4 displays the activity of 7% Pd/WA30 and some selected heterogeneous catalysts for hydrogenation. The reducible functionalities in each frame could be reduced using the corresponding catalyst. 7% Pd/WA30 catalyzed the hydrogenation of a relatively large number of functionalities, except for TBS ethers, benzyl alcohols, and aliphatic benzyl ethers.[34] Although the activity of 7% Pd/WA30 for hydrogenation was similar to that of Pd/C in the presence of amines or ammonium acetate as a moderate catalyst poison, the reaction never required the removal of such additives to obtain the pure product.

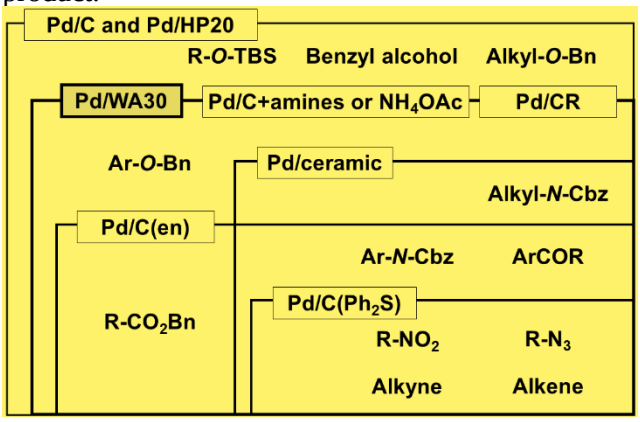


Fig. 4 Chemoselectivity of 7% Pd/WA30 in hydrogenation Pd/C(en) = Pd/C-ethylenediamine complex, Pd/C(Ph_2S) = Pd/C-diphenylsulfide complex.

Conclusion

We have developed a new heterogeneous palladium catalyst embedded in an anion exchange resin (WA30). *tert*-Amino functionalities on the WA30 skeleton act as an ancillary ligand for Pd species and accelerate the Suzuki–Miyaura coupling reaction using readily available chloroarenes. The 7% Pd/WA30-catalyzed coupling is also applicable to the coupling of heteroaryl chlorides and heteroaryl boronic acids. It was particularly important that less reactive 2-chloropyridines can be also applied to the 7% Pd/WA30-catalyzed Suzuki–Miyaura reaction. On the other hand 7% Pd/WA30-catalyzed hydrogenation at room temperature under ordinary hydrogen pressure could achieve the specific chemoselectivity induced by the moderate catalyst poison effect of WA30 *tert*-amino groups. The catalyst is recoverable by simple filtration. Although the activity of the recovered catalyst in the Suzuki–Miyaura reaction decreased because of its inevitable structural changes, 7% Pd/WA30 could be reused in hydrogenation, without any loss of the activity. Furthermore, it could be used for practical applications involving the wide range of utility in industries and reserch laboratories.

Experimental Section

General

All reagents and solvents were obtained from commercial sources and used without further purification. $Pd(OAc)_2$ was obtained from N.E. Chemcat Co. (Tokyo, Japan). Melting points (uncorrected) were determined on a Sansyo melting point apparatus SMP-300. IR spectra (neat) were measured using a Bruker Alpha FT-IR spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM ECA-500 (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR), ECS-400 (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR), or AL-400 (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) spectrometer. $CDCl_3$ or CD_3OD was used as the solvent for NMR measurement. Chemical shifts (δ) are expressed in part per million and internally referenced (0.00 ppm for tetramethylsilane for ^{1}H NMR and 77.0 ppm for ^{13}C NMR for $CDCl_3$, and 3.30 ppm for ^{1}H NMR and 49.0 ppm for ^{13}C NMR for CD_3OD). Mass spectra (EI) were taken on a JEOL JMS Q1000GC Mk II Quad GC/MS. High resolution mass spectra were measured by Shimadzu hybrid LCMS-IT-TOF (LCMS-IT-TOF). The Hitachi HD-2000 STEM, ULVAC-PHI PHI QuanteraSXM, Shimadzu ICPS-8100, and PANalytical X'Pert PRO-MPD were used for the scanning transmission electron microscope (STEM) analysis, X-ray photoelectron spectroscopy (XPS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and X-ray diffraction analysis (XRD), respectively. All of ^{1}H NMR spectra of known products were identical with those in the literature.

Typical procedure for the coupling reaction between aryl chlorides and arylboronic acids (Table 1)

This article is protected by copyright. All rights reserved.

Accepted Manuscript

7% Pd/WA30 (19.0 mg, 12.5 μmol), the aryl chloride (250 μmol), the arylboronic acid (375 μmol), Cs_2CO_3 (163 mg, 500 μmol) and DMA (1 mL) were added in a test tube. The mixture was stirred at 80 °C under Ar atmosphere. The reaction progress was monitored by thin layer chromatography (TLC) (hexane/EtOAc, 5:1). After complete consumption of the aryl chloride or 24 h (if the reaction was incomplete), the mixture was cooled to rt, diluted with Et_2O (5 mL), and filtered through a cotton filter. The catalyst on the filter was washed with Et_2O (15 mL × 2) and H_2O (10 mL × 3). The combined filtrates were separated into two layers. The aqueous layer was extracted with Et_2O (20 mL), and the combined organic layers were washed with H_2O (20 mL × 4) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. $CDCl_3$ (ca. 1 mL) and 1,4-dioxane (8.53 μL, 100 μmol) were added to the residue. After the determination of the reaction yield by ^1H NMR, the product was purified by silica gel column chromatography using hexane/EtOAc (10:1) as eluents to afford the corresponding biaryl.

Typical procedure for the synthesis of heterobiaryls (Table 2)

Conditions A: The conditions were the same as for the coupling between aryl chlorides and arylboronic acids. The residue was purified by silica gel column chromatography using hexane/EtOAc as eluents to afford the corresponding heterobiaryl.

Conditions B: 7% Pd/WA30 (19.0 mg, 12.5 μmol), the aryl chloride [or the heteroaryl chloride (250 μmol)], the aryl boronic acid [or the heteroaryl boronic acid (375 μmol)], K_3PO_4 (106 mg, 500 μmol) and *i*PrOH (1 mL) were added in a test tube. The mixture was stirred at 80 °C under Ar atmosphere. The reaction progress was monitored with TLC (hexane/EtOAc, 5:1). After complete consumption of the aryl chloride or after 24 h (if the reaction was incomplete), the mixture was cooled to rt, diluted with EtOAc (5 mL), and passed through a cotton filter. The catalyst on the filter was washed with EtOAc (15 mL × 2) and H_2O (10 mL × 3). The combined filtrates were separated into two layers. The aqueous layer was extracted with EtOAc (20 mL), and the combined organic layers were washed with H_2O (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the corresponding heterobiaryl.

Procedure for the mechanistic study (Table 3)

For entries 3–8: A mixture of Pd catalyst (12.5 μmol) and amine (87.5 μmol) in a test tube was stirred at room temperature under an Ar atmosphere. After 1 h, 4'-chloroacetophenone (32.4 μL, 250 μmol), phenylboronic acid (45.7 mg, 375 μmol), Cs_2CO_3 (163 mg, 500 μmol) and DMA (1 mL) was added to the mixture. It was stirred at 80 °C under an Ar atmosphere. After the specific time, the mixture was cooled to room temperature, diluted with Et_2O (5 mL), and passed through a cotton filter. The catalyst on the filter was washed with Et_2O (15 mL × 2) and H_2O (10 mL × 3). The combined filtrates were separated into two layers. The aqueous layer was extracted with Et_2O (20 mL), and the combined organic layers were washed with H_2O (20 mL × 4) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. $CDCl_3$ (ca. 1 mL) and 1,4-dioxane (8.53 μL, 100 μmol) as an internal standard were added to the residue, and the yield of **3a** was determined by ^1H NMR analysis.

For the entry 9: A mixture of 7% Pd/WA30 (19.0 mg, 12.5 μmol), 4'-chloroacetophenone (32.4 μL, 250 μmol), phenylboronic acid (45.7 mg, 375 μmol), Cs_2CO_3 (163 mg, 500 μmol), and TEMPO (3.9 mg, 25.0 μmol) in DMA (1 mL) in a test tube was stirred at 80 °C under an Ar atmosphere. After 6 h, the mixture was cooled to rt, diluted with Et_2O (5 mL), and passed through a cotton filter. The catalyst on the filter was washed with Et_2O (15 mL × 2) and H_2O (10 mL × 3). The combined filtrates were separated into two layers. The aqueous layer was extracted with Et_2O (20 mL), and the combined organic layers were washed with H_2O (20 mL × 4) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. $CDCl_3$ (ca. 1 mL) and 1,4-dioxane (8.53 μL, 100 μmol) as an internal standard were added to the residue, and the yield of **3a** was determined by ^1H NMR analysis.

Typical procedure for the hydrogenation reaction (Table 4)

A mixture of the substrate (250 μmol) and 7% Pd/WA30 (3.8 mg, 2.50 μmol) in MeOH (1 mL) was stirred under H_2 atmosphere (balloon) at room temperature. After a specific time, the mixture was passed through a cotton filter. The catalyst on the filter was washed with MeOH (5 mL × 3). The filtrate was concentrated in vacuo to afford the corresponding spectrometrically pure reduced product. If the reaction was incomplete after 24 h, the temperature was raised to 40 or 50 °C.

Reuse test of 7% Pd/WA30 in hydrogenation (Table 5)

For the first run shown in Table 1, a mixture of cinnamyl alcohol (335 mg, 2.50 mmol) and 7% Pd/WA30 (38.0 mg, 25.0 μmol) in MeOH (10 mL) was stirred under H_2 atmosphere (balloon). After 5 h, the mixture was filtered using a Kiriyama funnel (1 μm filter paper). The catalyst on the filter was washed with EtOAc (3 mL × 5), and the filtrate was concentrated in vacuo to afford 3-phenyl-1-propanol in 100% yield (342 mg, 2.51 mmol). The recovered catalyst was dried at room temperature under reduced pressure overnight, and then weighed (36.9 mg, 97 % recovery). The reaction for the second run was carried out similarly to the first run except for the amount of cinnamyl alcohol (326 mg, 2.43 mmol) and 7% Pd/WA30 (36.9 mg, 24.3 μmol). 3-Phenyl-1-propanol was obtained in 100% yield (330 mg, 2.42 mmol). The reactions for the runs 3–5 were also carried out in a manner similar to the first run except for the amount of the substrate and the catalysts used. The results are summarized in the Supporting information.

Acknowledgements

This work was partially supported by JSPS KAKENHI Grant number 15K07863. We sincerely appreciate the N. E. Chemcat Co. and Mitsubishi Chemical Co. for providing the $Pd(OAc)_2$ and DIAION WA30, respectively.

References

[1] a) L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133–173; b) M. J. Climent, A. Corma, S. Iborra, *Chem. Rev.* **2011**, *111*, 1072–1133; c) A. Molnár, *Chem. Rev.* **2011**, *111*, 2251–2320; d) I. Hussain, J. Capricho, M. A. Yawer, *Adv. Synth. Catal.* **2016**, *358*, 3320–3349.

[2] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483.

[3] N. Miyaura, K. Yamada, A. Suzuki. *Tetrahedron Lett.* **1970**, *20*, 3437–3440.

[4] a) Y.–X. Ye, W.–L. Liu, B.–H. Ye, *Catal. Commun.* **2017**, *89*, 100–105; b) T. Li, Y. Liu, F.–S. Liu, *Appl. Clay Sci.* **2017**, *136*, 18–25; c) G. J. Lichtenegger, M. Maier, M. Hackl, J. G. Khinast, W. Gössler, T. Griesser, V. S. Phani Kumar, H. Gruber–Woelfler, P. A. Deshpande, *J. Mol. Cat. A* **2017**, *426*, 39–51; d) Y.

This article is protected by copyright. All rights reserved.

Accepted Manuscript

Wang, C. Lu, G. Yang, Z. Chen, J. Nie, *React. Funct. Polym.* **2017**, *110*, 38–46; e) H. Keypour, S. G. Saremi, M. Norozi, H. Veisi, *Appl. Org. Chem.* **2017**, *31*, e3558; f) J. Jansa, T. Řezníček, R. Jambor, F. Bureš, A. Lyčka, *Adv. Synth. Catal.* **2017**, *359*, 339–350; g) A. K. Sharma, H. Joshi, R. Bhaskar, S. Kumar, A. K. Singh, *Dalton Trans.* **2017**, *46*, 2485–2496; i) L. You, W. Zhong, G. Xiong, F. Ding, S. Wang, B. Ren, I. Dragutan, V. Dragutan, Y. Sun, *Appl. Catal. A* **2016**, *511*, 1–10; j) R. S. B. Gonçalves, A. B. V. de Oliveira, H. C. Sindra, B. S. Archanjo, M. E. Mendoza, L. S. A. Carneiro, C. D. Buarque, P. M. Esteves, *ChemCatChem* **2016**, *8*, 743–750.

[5] a) Y. Kitamura, S. Sako, T. Udzu, A. Tsutsui, T. Maegawa, Y. Monguchi, H. Sajiki, *Chem. Commun.* **2007**, 5069–5071; b) Y. Monguchi, Y. Fujita, K. Endo, S. Takao, M. Yoshimura, Y. Takagi, T. Maegawa, H. Sajiki, *Chem. Eur. J.* **2009**, *15*, 834–837; c) Y. Kitamura, S. Sako, A. Tsutsui, Y. Monguchi, T. Maegawa, Y. Kitade, H. Sajiki, *Adv. Synth. Catal.* **2010**, *352*, 718–730; d) Y. Monguchi, K. Sakai, K. Endo, Y. Fujita, M. Niimura, M. Yoshimura, T. Mizusaki, Y. Sawama, H. Sajiki, *ChemCatChem* **2012**, *4*, 546–558; e) T. Hattori, A. Tsubone, Y. Sawama, Y. Monguchi, H. Sajiki, *Catalysts* **2015**, *5*, 18–25.

[6] a) A. Ohtaka, E. Sakaguchi, T. Yamaguchi, G. Hanasaka, Y. Uozumi, O. Shimomura, R. Nomura, *ChemCatChem* **2013**, *5*, 2167–2169; b) B. Yuan, Y. Pan, Y. Li, B. Yin, H. Jiang, *Angew. Chem.* **2010**, *122*, 4148–4152; *Angew. Chem. Int. Ed.* **2010**, *49*, 4054–4058; c) G. Li, H. Yang, W. Li, G. Zhang, *Green Chem.* **2011**, *13*, 2939–2947; d) B. Karimi, P.F. Akhavan, *Inorg. Chem.* **2011**, *50*, 6063–6072; e) V. Pandarus, D. Desplantier-Giscard, G. Gingras, F. Béland, R. Ciriminna, M. Pagliaro, *Org. Process Res. Dev.* **2013**, *17*, 1492–1497; f) Y. M. A. Yamada, S. M. Sarkar, Y. Uozumi, *J. Am. Chem. Soc.* **2012**, *134*, 3190–3198; g) D.-H. Lee, M. Choi, B.-W. Yu, R. Ryoo, A. Taher, S. Hossain, M.-J. Jin, *Adv. Synth. Catal.* **2009**, *351*, 2912–2920; h) M. Adib, R. Karimi-Nami, H. Veisi, *New. J. Chem.* **2016**, *40*, 4945–4951; i) B. J. Gallon, R. W. Kojima, R. B. Kaner, P. L. Diaconescu, *Angew. Chem.* **2007**, *119*, 7389–7392; *Angew. Chem. Int. Ed.* **2007**, *46*, 7251–7254; j) R. Hashemi Fath, S. J. Hoseini, *J. Organomet. Chem.* **2017**, *828*, 16–23; k) Y. Uozumi, Y. Matsuura, T. Suzuka, T. Arakawa, Y. M. A. Yamada, *Synthesis* **2017**, *49*, 59–68.

[7]a) L. Wu, B.-L. Li, Y.-Y. Huang, H.-F. Zhou, Y.-M. He, Q.-H. Fan, *Org. Lett.* **2006**, *8*, 3605–3608; b) H. Li, P. Wang, H. Tang, J. Niu, J. Ma, *New. J. Chem.* **2015**, *39*, 4343–4350.

[8] HP20 has a very high surface area (≈590 m^2 g^{-1}) and fine pore structures (30 nm of radius). The pore size of HP20 is 1.3 mL g^{-1}. The Pd loading of Pd/HP20 was determined to be 10 wt% using ICP-AES. The XRD analysis revealed that the particle size of Pd species in the 10% Pd/HP20 was 4 nm and the most of Pd species exist as Pd(0) metal. The EPMA of Pd/HP20 indicated the uniform distribution of Pd metal on the support. For detail characterization of 10% Pd/HP20, see ref. 5b. For detail information of DIAION HP20, also see http://www.diaion.com/en/products/synthetic_adsorbents/.

[9] H. Sajiki, Y. Monguchi in *Pharmaceutical Process Chemistry* (Eds.: T. Shioiri, K. Izawa, T. Konoike), Wiley-VCH, Weinheim, **2010**, pp 77–99.

[10] H. Sajiki, *J. Org. Synth. Chem. Jpn.* **2014**, *72*, 39–50.

[11] R. C. Larock, *Comprehensive Organic Transformations 2nd ed.*, WILEY-VCH, New York, **1999**.

[12] S. Nishimura, *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, Wiley-Interscience, New York, **2001**.

[13] M. Hudlickey, *Reduction in Organic Chemistry 2nd ed.*, American Chemical Society, Washington, D.C., **1996**.

[14] P. N. Rylander, *Hydrogenation Methods*, Academic Press, New York, **1985**.

[15] H. Lindlar, R. Dubuis, *Org. Synth. Coll. Vol. 5*, **1973**, 880–882.

[16] a) H. Hagiwara, T. Nakamura, T. Hoshi, T. Suzuki, *Green Chem.* **2011**, *13*, 1133–1137; b) J. Le Bras, D. K. Mukherjee, S. González, M. Tristany, B. Ganchegui, M. Moreno–Mañas, R. Pleixats, F. Hénin, J. Muzart, *New J. Chem.* **2004**, *28*, 1550–1553; c) A. Nagemdiran, V. Pascan, A. Bermejo Gomez, G. Gonzalez Miera, C.–W. Tai, O. Verho, B. Martin–Matute, J.–E. Bäckvall, *Chem. Eur. J.* **2016**, *22*, 7184–7189; d) A. Dasgupta, V. Rarrmkumar, S. Sankararaman, *RSC Adv.* **2015**, *5*, 21558–21561; e) Z. S. Qureshi, P. B. Sarawade, M. Albert, V. D'Elia, M. N. Hedhili, K. Köhler, J.–M. Basset, *ChemCatChem* **2015**, *7*, 635–642; f) T. Mitsudome, T. Urayama, K. Yamazaki, Y. Maehara, J. Yousuke, K. Gohara, Z. Maeno, T. Mizugaki, K. Jitsukawa, K. Kaneda, *ACS Catal.* **2016**, *6*, 666–670; g) A. Ota, M. Armbrüster, M. Behrens, D. Rosenthal, M. Friedrich, I. Kasatkin, F. Girgsdies, W. Zhang, R. Wagner, R. Schlögl, *J. Phys. Chem. C* **2011**, *115*, 1368–1374; h) M. W. Tew, H. Emerich, J. A. van Bokhoven, *J. Phys. Chem. C* **2011**, *115*, 8457–8465; i) Z. Shao, C. Li, X. Chen, M. Pang, X. Wang, C. Liang, *ChemCatChem* **2010**, *2*, 1555–1558; j) M. Armbrüster, K. Kovnir, M. Behrens, D. Teschner, Y. Grin, R. Schlögl, *J. Am. Chem. Soc.* **2010**, *132*, 14745–14747; k) J. Hori, K. Murata, T. Sugai, H. Shinohara, R. Noyori, N. Arai N. Kurono T. Ohkura, *Adv. Synth. Catal.* **2009**, *351*, 3143–3149; l) P. Weerachawanasak, O. Mekasuwandumrong, M. Arai, S.–I. Fujita, P. Praserthdam, J. Panpranot, *J. Catal.* **2009**, *262*, 199–205; m) N. M. Callis, E. Thiery, J. Le Bras, L. Muzart, *Tetrahedron Lett.* **2007**, *48*, 8128–8131; n) S. Yang, C. Cao, L. Peng, J. Zhang, B. Han, W. Song, *Chem. Commun.* **2016**, *52*, 3627–3630; o) S. Domínguez–Domínguez, Á. Berenguer-Murcia, B. K. Pradhan, Á. Linares–Solano, D. Cazorla–Amorós, *J. Phys. Chem. C* **2008**, *112*, 3827–3834; p) C. Liu, H. Bao, D. Wang, X. Wang, Y. Li, Y. Hu, *Tetrahedron Lett.* **2015**, *56*, 6460–6462; q) M. V. Vasylyev, G. Maayan, Y. Hovav, A.

This article is protected by copyright. All rights reserved.

Accepted Manuscript

Haimov, R. Neumann, *Org. Lett.* **2006**, *8*, 5445–5448; r) K. D. Kim, S. Pokhrel, Z. Wang, H. Ling, C. Zhou, Z. Liu, M. Hunger, L. Mädler, J. Huang, *ACS Catal.* **2016**, *6*, 2372–2381; s) S. Zhang, C.–R. Chang, Z.–Q. Huang, J. Li, Z. Wu, Y. Ma, Z. Zhang, Y. Wang, Y. Qu, *J. Am. Chem. Soc.* **2016**, *138*, 2629–2637; t) J. Tuteja, S. Nishimura, K. Ebitani, *RSC Adv.* **2014**, *4*, 38241–38249; u) W. Chen, H. Bao, D. Wang, X. Wang, Y. Li, Y. Hu, *Tetrahedron* **2015**, *71*, 9240–9244; v) Z. Wu, H. Jiang, *RSC. Adv.* **2015**, *5*, 34622–34629.

[17] H.–Y. Lee, S. Ryu, H. Kang, Y. Jun, J. Chen, *Chem. Commun.* **2006**, 1325–1327.

[18] a) H. Sajiki, K. Hirota, *Tetrahedron* **1998**, *54*, 13981–13996; b) H. Sajiki, K. Hirota, *J. Org. Synth. Chem. Jpn.* **2001**, *59*, 109–120; c) A. Mori, T. Mizusaki, M. Kawase, T. Maegawa, Y. Monguchi, S. Takao, Y. Takagi, H. Sajiki, *Adv. Synth. Catal.* **2008**, *350*, 406–410; d) Y. Monguchi, T. Marumoto, T. Ichikawa, Y. Miyake, Y. Nagae, M. Yoshida, Y. Oumi, Y. Sawama, H. Sajiki, *ChemCatChem* **2015**, *7*, 2155–2160; e) Y. Monguchi, T. Ichikawa, H. Sajiki, *Chem. Pharm. Bull.* **2017**, *65*, 2–9; f) Y. Monguchi, F. Wakayama, S. Ueda, R. Ito, H. Takada, H. Inoue, A. Nakamura, Y. Sawama, H. Sajiki, *RSC. Adv.* **2017**, *7*, 1833–1840; g) Y. Kitamura, A. Tanaka, M. Sato, K. Oono, T. Ikawa, T. Maegawa, Y. Monguchi, H. Sajiki, *Synth. Commun.* **2007**, *37*, 4381–4388; h) Y. Yabe, Y. Sawama, Y. Monguchi, H. Sajiki, *Catal. Sci. Technol.* **2014**, *4*, 260–271; i) A. Kawanishi, C. Miyamoto, Y. Yabe, M. Inai, T. Asakawa, Y. Hamashima, H. Sajiki, T. Kan, *Org. Lett.* **2013**, *15*, 1306–1309; j) T. Takahashi, M. Yoshimura, H. Suzuka, T. Maegawa, Y. Sawama, Y. Monguchi, H. Sajiki, *Tetrahedron* **2012**, *68*, 8293–8299; k) Y. Yabe, Y. Sawama, T. Yamada, S. Nagata, Y. Monguchi, H. Sajiki, *ChemCatChem* **2013**, *5*, 2360–2366; l) Y. Monguchi, T. Ichikawa, K. Nozaki, K. Kihara, Y. Yamada, Y. Miyake, Y. Sawama, H. Sajiki, *Tetrahedron* **2015**, *71*, 6499–6505.

[19] http://www.diaion.com/en/products/index.html

[20] The physical properties of DIAION WA30 were summarized in the following table.

The amount of amino functionalities	Surface area	Pore volume
4.96 mmol g^{-1}	15 m^2 g^{-1}	1.3 mL g^{-1}

[21] Y. Monguchi, T. Ichikawa, M. Netsu, T. Hattori, T. Mizusaki, Y. Sawama, H. Sajiki, *Synlett* **2015**, *26*, 2014–2018.a

[22] The Pd loading of Pd/WA30 was determined to be 7 wt% by the measurement of Pd species in the filtrates obtained after the adsorption process and reduction process using the atom absorption spectrometry, see ref. 21.

[23] The molar ratio of Pd species vs. *tert*-amino group in 7% PdWA30 was calculated to be 1 : 7 (Pd/*tert*-amine). 70/106.42 (mmol) : 4.96 × (1–0.07) (mmol) = 1 : 7.01 (in the case of 1.0 g of 7% Pd/WA30).

[24] The particle size was estimated to be 3–4.2 nm by the peak of (1,1,1), (2,0,0), and (2,2,0) faces of Pd species.

	2θ/degree	$B_{obs.}$ /degree	$B_{struct.}$ /degree	diameter/nm
(1,1,1)	39.862	2.062	1.992	4.2
(2,0,0)	46.288	2.971	2.900	3.0
(2,2,0)	67.827	3.047	2.968	3.2

[25] In the cases of the synthesis of **3b**, **3c**, **3g**, **3h**, and **3k**, the usage of arylboronic acids was increased due to the less reactivity of the corresponding aryl chlorides (**2**).

[26] Since the molar ratio of *tert*-amino group on WA30 to Pd species on 7% Pd/WA30 is 7 : 1 (see ref. 23), 7 equiv of amines to Pd species of 10% Pd/HP20 was added.

[27] Q. Liu, X. Dong, J. Li, J. Xiao, Y. Dong, H. Liu *ACS Catal.* **2015**, *5*, 6111–6137.

[28] F. Proutiere, M. Aufiero, F. J. Shoenbeck, *J. Am. Chem. Soc.* **2012**, *134*, 606–612.

[29] Z. Feng, Q.–Q. Min, Y.–L. Xiao, B. Zhang, X. Zhang, *Angew. Chem.* **2014**, *126*, 1695–1699; *Angew. Chem. Int. Ed*. **2014**, *53*, 1669–1673.

[30] H. Stadtmullar, A. Vaupel, C. E. Tucker, T. Stüdemann, P. Knochel, *Chem. Eur. J.* **1996**, *2*, 1204–1220.

[31] A. S. Dudnik, G. C. Fu, *J. Am. Chem. Soc.* **2012**, *134*, 10693–10697.

[32] F. González–Bobes, G. C. Fu, *J. Am. Chem. Soc.* **2006**, *128*, 5360–5361.

[33]a) A. Mori, T. Mizusaki, T. Ikawa, T. Maegawa, Y. Monguchi, H. Sajiki, *Chem. Eur. J.* **2007**, *13*, 1432–1441; b) Y. Monguchi, A. Kume, H. Sajiki, *Tetrahedron* **2006**, *62*, 8384–8392.

[34] Similar chemoselective hydrogenations could be achieved by the use of palladium catalysts supported on chelate resins (Pd/CR11 and Pd/CR20), see ref. 18e and 18l.

Accepted Manuscript

This article is protected by copyright. All rights reserved.

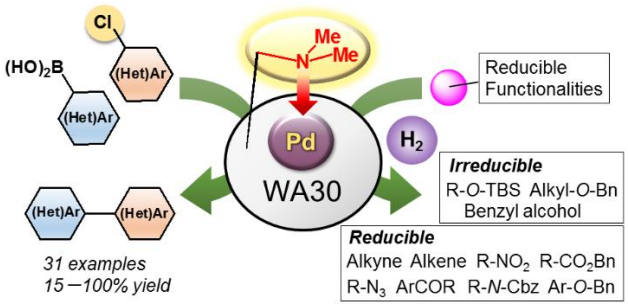
10.1002/adsc.201700156

FULL PAPER

Development of a unique heterogeneous palladium catalyst for Suzuki–Miyaura reaction using (hetero)aryl chlorides and chemoselective hydrogenation

Adv. Synth. Catal. **Year**, *Volume*, Page – Page

Tomohiro Ichikawa,[a] Moeko Netsu,[a] Masahiro Mizuno,[a] Tomoteru Mizusaki,[b] Yukio Takagi,[b] Yoshinari Sawama,[a] Yasunari Monguchi[a]* and Hironao Sajiki[a]*



Accepted Manuscript

This article is protected by copyright. All rights reserved.