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Development of chelate resin-supported palladium catalysts for chemoselective hydrogenation

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ABSTRACT

Two kinds of palladium catalysts immobilized on a chelate resin bearing diiminoacetate or polyamine moieties on the polystyrene-divinylbenzene polymer were newly prepared by the adsorption of palladium (II) ions on these resins followed by the reduction to palladium (0) with hydrazine monohydrate. Both catalysts showed a similar activity for hydrogenation. A variety of reducible functionalities, except for benzylic alcohol, alkyl benzyl ether, silyl ether, and epoxide, could be reduced under the hydrogenation conditions using either catalyst. Since the palladium metal elution from the immobilized catalysts was never observed, the catalysts could be reused without any decrease in the catalyst activity for at least 5 runs.

1. Introduction

The selective hydrogenation of specific functional groups in the coexistence of multiple functionalities within a molecule is an important technology in synthetic organic chemistry, since it is strongly correlated with the development of new synthetic routes and shortening of the synthetic pathway.[1] Chemoselective hydrogenation is conventionally achieved by the addition of catalyst poisons to control the catalyst activity.[2] We have utilized nitrogen containing bases[3] and diphenylsulfide[4] as the appropriate catalyst poison additives to the palladium-on-carbon (Pd/C)-catalyzed hydrogenation system to establish several procedures for the chemoselective method. Furthermore, such additives could also be immobilized on Pd/C by complexation due to the coordinative ability to the palladium metal, and the newly developed catalysts all have their distinctive catalyst activities.[5] It is known that the activity of heterogeneous palladium catalysts are affected by the characteristics of the support itself that allow the chemoselectivity under hydrogenation conditions, but only a few catalysts were reported to have a general use[6] execept for the semi-hydrogenation of disubstituted alkynes to *cis*-alkenes.[6h–s] We have developed heterogeneous and chemoselective palladium catalysts for the hydrogenation, which were embedded on silk fibroin,[7] polyethylene imine,[8] molecular sieves,[9] boron nitride,[10] and synthetic adsorbents[11] as the supports, and specific chemoselective hydrogenation methods were provided due to the difference in catalyst activities based on the properties of each support.

DIAION CR11 and CR20, commercially available chelate resins (Mitsubishi Chemical Corporation), bearing diiminoacetate and polyamine moieties, respectively, as chelating functionalities on the polystyrene-divinylbenzene-based copolymer have long been utilized as water purifiers based on the capture ability of metal ions.[12] We recently successfully developed copper catalysts for the solvent-free Huisgen cyclization to generate 1,4-disubstituted triazoles from azides and alkynes and osmium catalysts for the oxidation of alkenes to diols, both of which were supported on the CR 11 and CR20 by immersing them in an aqueous solution of $Cu(NH_3)_2 \cdot 3H_2O$ and a methanolic solution of OsO_4, respectively.[13] The immobilization of palladium (II) metal on the diiminoacetate-based chelate resin, DIAION CR10, which was previously commercially available from the Mitsubishi Chemical Corporation, has been

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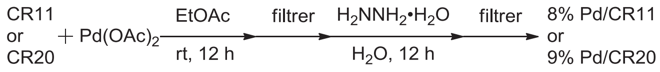
studied by Hirai and Toshima,[14] and Pd(II)/CR10 exhibited a hydrogenation catalyst activity toward cyclopentadiene,[14a,b] cyclooctadiene,[14c,d] and acrylic acid.[14c] The DIAION CR11 has a higher surface area, pore size, and pore volume when compared to DIAION CR10,[15] which would increase the efficiency based on the absorption (enrichment) effect of the substrates on DIAION CR11, leading to an enhancement of the catalyst activity.

In this paper, we describe the new development of heterogeneous palladium catalysts supported on CR11 and CR20 and an application for a novel and chemoselective hydrogenation method.

2. Results and discussion

2.1. Preparation and characterization of Pd/CR11 and Pd/CR20

The palladium (0) species were embedded on the chelate resins by a sequential process via adsorption and reduction of Pd(II) Scheme 1. The CR11 and CR20 were immersed in an EtOAc solution of $Pd(OAc)_2$ at room temperature and gently stirred for 12 h. The rust-colored solution was almost totally decolored after the stirring, and the white resins changed to yellow. They were collected by filtration, sequentially washed with EtOAc, H_2O, and MeOH, dried under reduced pressure, then stirred in an aqueous solution of hydrazine monohydrate at room temperature for 12 h. The resulting black catalysts, Pd/CR11 and Pd/CR20, were collected by filtration, washed with MeOH and H_2O, and dried under reduced pressure. The palladium contents of the 8 wt % Pd/CR11 and 9 wt % Pd/CR20 were calculated based on the concentration of the residual Pd in each filtrate, which was determined by atomic absorption spectrometry.



Scheme 1. Preparation method of chelate resin-supported palladium catalysts (Pd/CR11 and Pd/CR20).

The diameters of the Pd clusters of the 8% Pd/CR11 and 9% Pd/CR20 were determined to be approximately 15 nm and 10 nm, respectively, from the images of the catalyst surfaces, which were obtained by high-angle annular dark-field scanning transmission electron microscopy (HAADF–STEM) (Fig. 1). An electron probe microanalysis (EPMA) indicated that the palladium species of both catalysts are mainly located on the catalyst surface, and almost no palladium species are found in a deep layer of the 8% Pd/CR11 (Fig. 2).[16] The oxidation states of the palladium species of both catalysts were determined by X-ray photoelectron spectroscopy (XPS, Fig. 3). The spectra of the 8% Pd/CR11 and 9% Pd/CR20 were similar and showed the highest peaks at ca. 340.6 and 335.5 eV as $Pd3d_{3/2}$ and $Pd3d_{5/2}$, respectively, for the Pd(0) species with shoulder peaks at ca. 342.5 and 336.9 for the Pd(II) species, indicating that both catalysts mainly consist of Pd(0) species, but include a small amount of Pd(II) species.

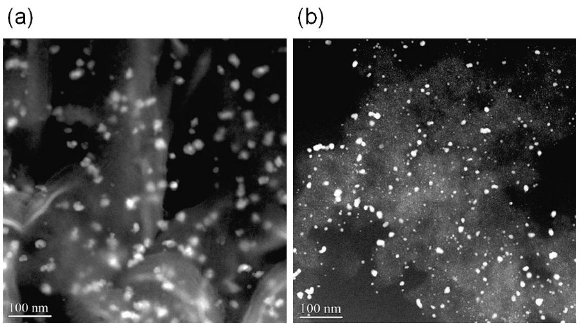


Fig. 1. (a) HAADF–STEM images of 8% Pd/CR11 and (b) 9% Pd/CR20.

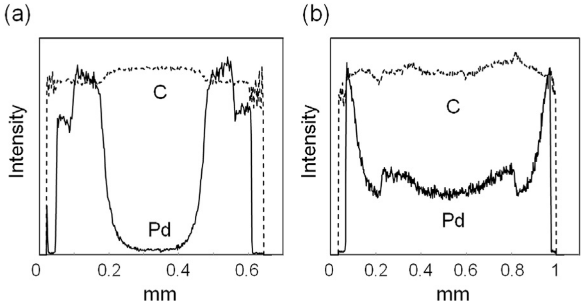


Fig. 2. (a) EPMA of 8% Pd/CR11 and (b) 9% Pd/CR20.

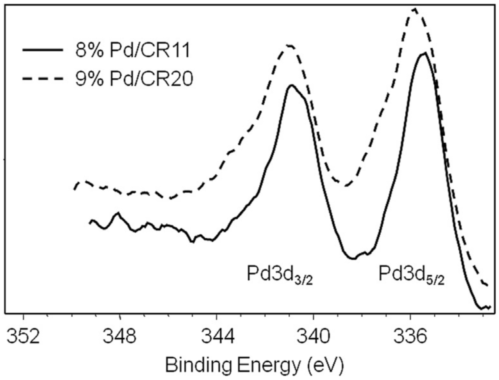


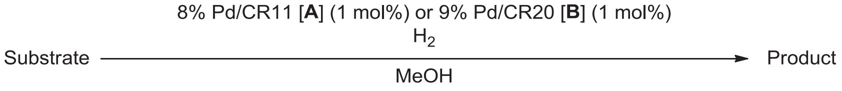
Fig. 3. XPS spectra of 8% Pd/CR11 and 9% Pd/CR20.

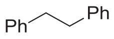
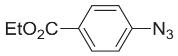
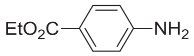
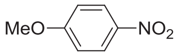
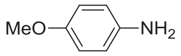
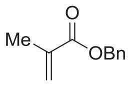
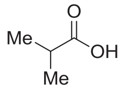
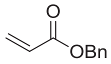
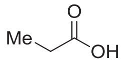
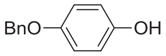
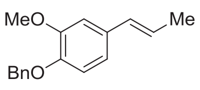
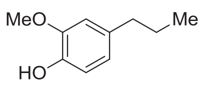
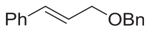
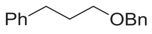
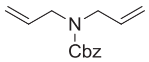
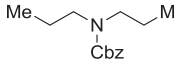
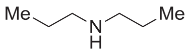
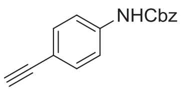
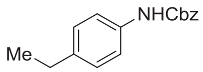
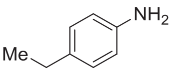
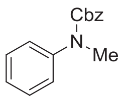
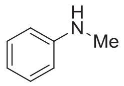
2.2. 8% Pd/CR11 and 9% Pd/CR20 as hydrogenation catalysts

The catalyst activity of 8% Pd/CR11 and 9% Pd/CR20 for the hydrogenation was evaluated using substrates possessing a variety of reducible functionalities within the molecule in MeOH. When the reactions were incomplete at room temperature under ordinary hydrogen pressure, the reaction temperature was raised to 40 or 50 °C. When the optimization was insufficient under pressurized hydrogen, the optimal temperature was investigated under two hydrogen conditions (3 or 5 atm). The results are summarized in Table 1. The hydrogenation of alkyne (Entries 1, 2, and 21–25), azido (Entries 3 and 4), nitro (Entries 5 and 6), alkene (Entries 7–10, 13–20, and 38–41), benzyl ester (Entries 7–10), and aryl benzyl ether (Entries 11–14) functionalities smoothly proceeded at room temperature under ordinary hydrogen pressure. The *N*-Cbz protecting groups of both the aliphatic and aromatic amines could be removed (Entries 17–27); heat or pressurized hydrogen was applied when the substrates were relatively inert. On the other hand, the alkyl benzyl ether was never deprotected (Entries 15 and 16), while the coexisting alkene could be reduced to the corresponding alkane. The aromatic aldehyde was completely and selectively hydrogenated to the corresponding benzylalcohol derivatives without the hydrogenolysis of the benzylic hydroxyl group (Entries 28 and 29). Although aromatic ketones were quite stable at 40 °C (for isobutylophenone) or 50 °C (for acetophenone) under atmospheric hydrogen conditions, the corresponding *sec*-benzylalcohols could be quantitatively obtained by tuning the temperature and/or hydrogen pressure (Entries 30–37). It is noteworthy that the hydrogenolysis of the benzylic hydroxyl groups never took place even at 50 °C under 3 or 5 atm of H_2 pressure (Entries 35 and 37), and both catalysts were inactive for the hydrogenation of silyl ethers, including the relatively labile triethylsilyl ether (Entries 38–41).

Furthermore, the 8% Pd/CR11 and 9% Pd/CR20 indicated very low catalyst activities for the hydrogenolysis of epoxides, and only 10–15% of the epoxide ring was cleaved in MeOH after 24 h when

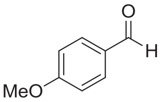
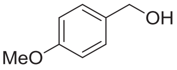
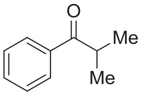
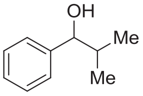
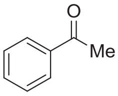
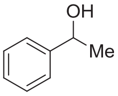
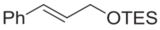
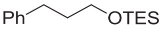
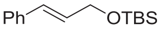
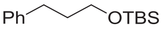
Table 1
8% Pd/CR11-and 9% Pd/CR20-catalyzed hydrogenation



Entry	Substrate	Catalyst	H_2 pressure (atm)	Temp(°C)	Time (h)	Product	Ratio[a] SM:1:2
1		**A**	1	rt	6		0:100 (100)
2		**B**	1	rt	6		0:100 (99)
3		**A**	1	rt	6		0:100 (100)
4		**B**	1	rt	6		0:100 (100)
5		**A**	1	rt	4.5		0:100 (93)
6		**B**	1	rt	7		0:100 (100)
7[b]		**A**	1	rt	24		0:100
8[b]		**B**	1	rt	24		0:100
9[b]		**A**	1	rt	24		0:100
10[b]		**B**	1	rt	24		0:100
11		**A**	1	rt	18		0:100 (100)
12		**B**	1	rt	18		0:100 (96)
13		**A**	1	rt	24		0:100 (100)
14		**B**	1	rt	24		0:100 (100)
15		**A**	1	rt	24		0:100 (100)
16		**B**	1	rt	24		0:100 (98)
17[b]		**A**	1	rt	24	 **1**  **2**	0:9:91
18[b]		**A**	3	rt	24		0:0:100
19[b]		**B**	1	rt	24		0:70:30
20[b]		**B**	3	rt	24		0:0:100
21		**A**	1	rt	24	 **1**  **2**	0:63:37
22		**A**	1	40	24		0:2:98
23		**A**	1	50	24		0:0:100 (100)
24		**B**	1	rt	24		0:68:32
25		**B**	1	40	24		0:0:100 (100)
26		**A**	1	rt	24		0:100 (85)
27		**B**	1	rt	24		0:100 (66)

(*continued on next page*)

Table 1 (*continued*)

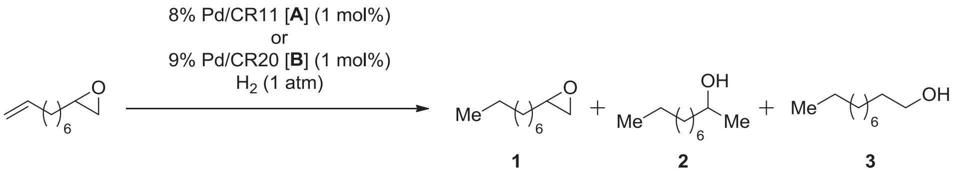
Entry	Substrate	Catalyst	H_2 pressure (atm)	Temp(°C)	Time (h)	Product	Ratio[a] SM:1:2
28		**A**	3	rt	24		0:100 (86)
29		**B**	3	rt	24		0:100 (99)
30		**A**	1	40	24		2:98
31		**A**	1	50	24		0:100 (100)
32		**B**	1	40	24		7:93
33		**B**	3	rt	24		0:100 (85)
34		**A**	1	50	24		12:88
35		**A**	3	50	24		0:100 (96)
36		**B**	1	50	24		31:68
37		**B**	5	50	24		0:100 (94)
38		**A**	1	rt	24		0:100 (94)
39		**B**	1	rt	24		0:100 (94)
40		**A**	1	rt	24		0:100 (100)
41		**B**	1	rt	24		0:100 (100)

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

[b] The reaction was performed in CD_3OD as the solvent to directly determine the ratio of the volatile starting material and/or products by ^1H NMR.

Table 2

Stability of epoxide under the 8% Pd/CR11-and 9% Pd/CR20-catalyzed hydrogenation conditions



Entry	Catalyst	Solvent	Time (h)	Ratio[a] 1: 2: 3
1	**A**	MeOH	24	84:11:5
2	**A**	MeOH	3	92:trace:8
3	**A**	EtOAc	5	97:0:3
4	**A**	THF	5	<100:0:trace
5	**A**	1,4-dioxane	9	100 (97)[b]:0:0
6	**B**	MeOH	24	89:9:2
7	**B**	MeOH	3	98:0:2
8	**B**	1,4-dioxane	8	100 (99)[b]:0:0

[a] Ratio was determined by ^1H NMR.

[b] Isolated yields are indicated in parentheses.

2-epoxy-9-decene was used as the substrate (Table 2, Entries 1 and 6). While the hydrogenative ring-opening reaction of the epoxide was significantly observed even after 3 h (Entries 2 and 7), the development of a total suppression method of the ring opening of the epoxide was investigated using the coordinative ability of ethereal solvents for the 8% Pd/CR11-catalyzed hydrogenation due to the appropriate poisonous effect of the bulk ethereal solvent.[17–19] While a very small amount of alcohols were generated in EtOAc or THF (Table 2, Entries 3 and 4), the selective hydrogenation of only the alkene in the presence of an epoxide could be achieved in 1,4-dioxane as the solvent (Table 2, Entry 5). A similar chemoselective hydrogenation was achieved in the case of 9% Pd/CR20 in 1,4-dioxane (Table 2, Entry 8). Furthermore, the optimal conditions could be applied to the fully selective hydrogenation of the alkene moieties of 1,2-epoxy-7-octene and glycidyl methacrylate (Table 3).

The reuse of catalysts is an important issue from environmental and economical points of view. The reuse of the 8% Pd/CR11 and 9% Pd/CR20 was examined using diphenylacetylene as a substrate (Table 4). Both catalysts could be recovered and reused for at least 5 runs without any loss of catalyst activity. Furthermore, the leached palladium species in the filtrate after the same filtration (0.2 μm membrane filter) of the reaction mixture for the hydrogenation using cinnamyl alcohol as the substrate were never detected by inductively coupled plasma-atomic emission spectrometry (ICP-AES, detection limit: <1 ppm).

Table 3
Hydrogenation of alkenes in the presence of epoxides

$$\text{Substrate} \xrightarrow[\text{1,4-dioxane, rt}]{\substack{\text{8\% Pd/CR11 [A] (1 mol\%)} \\ \text{or} \\ \text{9\% Pd/CR20 [B] (1 mol\%)} \\ H_2 \text{ (1 atm)}}} \text{Product}$$

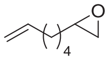
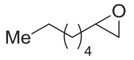
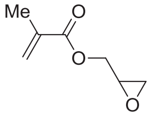
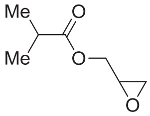
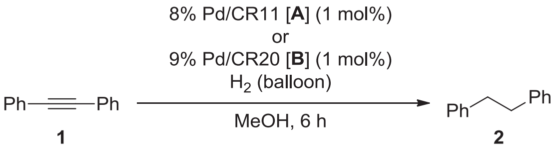
Entry	Substrate	Cat.	Time (h)	Product	Yield (%)
1		**A**	9		82
2		**B**	9		84
3		**A**	18		100
4		**B**	9		100

Table 4
Reuse of Pd/CR11 and Pd/CR20



1

2

Run	1st	2nd	3rd	4th	5th
Recovered **A** (%)	100	100	100	100	100
Yield (%)[a]	98	96	100	100	100
Recovered **B** (%)	100	100	96	98	98
Yield (%)[a]	97	97	98	99	99

[a] No starting material was recovered.

Fig. 4 shows the hydrogenation catalyst activity for various reducible functionalities. The functionalities in each frame could be reduced using the corresponding catalyst. The 8% Pd/CR11-and 9% Pd/CR20-catalyzed hydrogenations could specifically exclude the hydrogenolysis of the epoxide from the frame. Although a similar chemoselectivity was achieved by the Pd/C–NH_4OAc combined method, the present hydrogenation required no special procedure to remove the additives due to the totally heterogeneous catalytic conditions without any additives and Pd leaching.

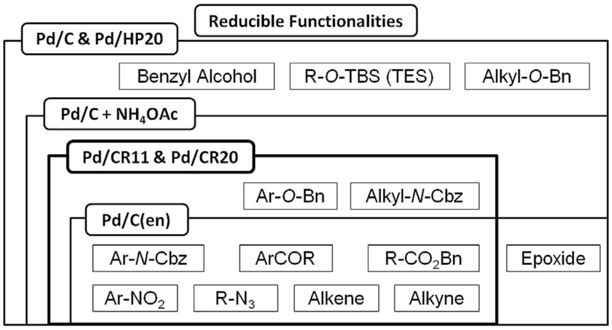


Fig. 4. Chemoselectivity of 8% Pd/CR11- and 9% Pd/CR20-catalyzed hydrogenations.

3. Conclusion

We have developed two types of heterogeneous palladium catalysts having very similar catalyst properties and activities when embedded on chelate resins, bearing diminoacetate moieties (CR11) or polyamine moieties (CR20) on the polystyrene-based polymers. Various kinds of reducible functionalities, such as alkyne, alkene, azide, nitro, benzyl ester, *N*-Cbz, aromatic carbonyl, and aryl benzyl ether functionalities, could be hydrogenated, while the hydrogenolysis of benzyl alcohols, silyl ethers, and alkyl benzyl ethers was hardly observed. The hydrogenative ring opening reaction of an epoxide could be suppressed in 1,4-dioxane as the solvent. Both catalysts could be reused for at least five runs without any loss of the catalyst activity. Since no palladium species were leached from the catalysts, they could be used for practical applications involving the chemoselective and low cost hydrogenations as environmentally-benign catalysts in industry and the laboratory. Pd/CR11 is now commercially available from Wako Pure Chemical Industries, Ltd. The product name and code numbers are as follows: palladium-iminodiacetic acid, 160-26571 (1 g) and 166-26573 (5 g).

4. Experimental section

4.1. 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). The ^1H NMR spectra were measured by a JEOL JMN AL-400 spectrometer (400 MHz) using $CDCl_3$ or CD_3OD as the solvent. Chemical shifts (δ) were expressed in parts per million and internally referenced (0.00 ppm for tetramethylsilane/$CDCl_3$ or 3.30 ppm for CD_3OD). HAADF–STEM, EPMA, and XPS were measured by a JEM-ARM200F (JEOL), JXA-8230 (JEOL), and JPS-9200 (JEOL), respectively.

4.2. Preparation of 8% Pd/CR11

A mixture of DIAION CR11 [2.00 g, water content 52.47%; 951 mg (net)] in a solution of $Pd(OAc)_2$ [174 mg, 0.775 mmol (82.5 mg, palladium quantity)] in EtOAc (8 mL) was stirred under an Ar atmosphere at rt for 12 h. The blown solid was collected on a Kiriyama funnel (1 µm), washed with EtOAc (5 mL×5), H_2O (5 mL×5), and MeOH (5 mL×5), and dried under vacuum for 12 h. The filtrate was concentrated in vacuo and then transferred to a 100 mL volumetric flask with H_2O. Its atomic absorption analysis detected no palladium species. The collected solid was then stirred with $NH_2NH_2 \cdot H_2O$ (117 mg, 2.33 mmol) in H_2O (8 mL) under Ar at rt for 12 h. The black solid was collected on a Kiriyama funnel (1 µm), washed with H_2O (5 mL×5) and MeOH (5 mL×5), then dried under vacuum for 12 h to produce the Pd/CR11 (988 mg). The filtrate was concentrated in vacuo and then transferred to a 100 mL volumetric flask with H_2O. Its atomic absorption analysis indicated that 0.88 ppm (8.8 µg) of the palladium species was present. The palladium amount, which was not captured on CR11, was found to be 8.8 µg, which means that the palladium ratio of Pd/CR11 was 8.3% [(82.5−0.088)/988×100].

4.3. Preparation of 9% Pd/CR20

A mixture of DIAION CR20 [1.78 g, water content 49.0%; 908 mg (net)] in a solution of $Pd(OAc)_2$ [190 mg, 0.846 mmol (90.0 mg, palladium quantity)] in EtOAc (4 mL) was stirred under an Ar atmosphere at rt for 5 d. The blown solid was collected on a Kiriyama funnel (1 µm), washed with H_2O (10 mL×3), and MeOH (10 mL×4), and dried under vacuum for 12 h. The filtrate was concentrated in vacuo and then transferred to a 100 mL volumetric flask with H_2O. Its atomic absorption analysis indicated the 15.9 ppm (1.59 mg) of palladium species included. The collected solid was then stirred with $NH_2NH_2\cdot H_2O$ (127 mg, 2.54 mmol) in H_2O (3 mL) under Ar at rt for 12 h. The blown solid was collected on a Kiriyama funnel (1 μm), washed with H_2O (10 mL×3) and MeOH (10 mL×4), then dried under vacuum for 12 h to produce the Pd/CR20 (989 mg). The filtrate was concentrated in vacuo and then transferred to a 100 mL volumetric flask with H_2O. No palladium species were detected by its atomic absorption analysis. The palladium ratio of Pd/CR20 was estimated to be 8.9% [(90.0−1.59)/989×100].

4.4. General procedure for the hydrogenation

A mixture of the substrate (0.250 mmol) and catalyst [8% Pd/CR11 (3.3 mg, 2.50 μmol) or 9% Pd/CR20 (3.0 mg, 2.50 μmol)] in MeOH (1 mL) was stirred under an H_2 atmosphere (balloon) at room temperature. After a specific time, the mixture was filtered through a membrane filter (0.45 or 0.2 μm), and the filtrate was concentrated in vacuo to give the corresponding spectrometrically-pure reduced product. If the reaction was not completed, the temperature was raised to 40 or 50 °C. If the reaction was still incomplete, the H_2 pressure was increased to 3 or 5 atm. All the products were known, and the ^{1}H NMR spectral data of the products were identical to those in the literature (see Supplementary data).

4.5. Reuse test of 8% Pd/CR11

Ten test tubes were prepared, and diphenylacetylene (44.6 mg, 0.250 mmol), 8% Pd/CR11 (3.3 mg, 2.50 μmol, 1 mol %), and MeOH (1 mL) were placed in each test tube. The mixture in each test tube was stirred under an H_2 atmosphere (balloon) at room temperature for 6 h, then all the mixtures were filtered using a Kiriyama funnel (1 μm filter paper). The catalyst on the filter paper was washed with EtOAc (10 mL),and the filtrate was concentrated in vacuo to give 1,2-diphenylethane in 98% yield (445 mg, 2.44 mmol). The recovered catalyst was dried at room temperature under reduced pressure for 12 h, then weighed [32.9 mg, 100%, 32.9 ÷ (3.3×10)×100]. The reaction for the second run was carried out in the same manner as the first run, but using eight test tubes [total substrate amount, 357 mg (44.6 mg×8), 2.00 mmol (0.250 mmol×8), total catalyst amount, 26.4 mg (3.3 mg×8)]. 1,2-Diphenylethane was obtained in 96% yield (350 mg, 1.92 mmol), and the catalyst was quantitatively recovered (26.8 mg). The reactions for the third to fifth runs were also carried out in the same manner as the first run except for the number of used test tubes. The results are summarized in the Supplementary data.

4.6. Reuse test of 9% Pd/CR20

Ten test tubes were prepared, and diphenylacetylene (44.6 mg, 0.250 mmol), 9% Pd/CR20 (3.0 mg, 2.50 μmol, 1 mol %), and MeOH (1 mL) were placed in each test tube. The mixture in each test tube was stirred under an H_2 atmosphere (balloon) at room temperature for 6 h, then all the mixtures were filtered using a Kiriyama funnel (1 μm filter paper). The catalyst on the filter paper was washed with EtOAc (10 mL),and the filtrate was concentrated in vacuo to give 1,2-diphenylethane in 97% yield (442 mg, 2.43 mmol). The recovered catalyst was dried at room temperature under reduced pressure for 12 h, then weighed [30.2 mg, 100%, 30.2 ÷ (3.0×10)×100]. The reaction for the second run was carried out in the same manner as the first run, but using eight test tubes [total substrate amount, 357 mg (44.6 mg×8), 2.00 mmol (0.250 mmol×8), total catalyst amount, 24.0 mg (3.0 mg×8)]. 1,2-Diphenylethane was obtained in 97% yield (352 mg, 1.93 mmol), and the catalyst was quantitatively recovered (23.9 mg). The reactions for the third to fifth run were also carried out in the same manner as the first run except for the number of used test tubes. The results are summarized in the Supplementary data.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.03.086.

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15. The general properties of DIAION CR10, CR11, and CR20 (Mitsubishi Chemical data).

	Surface area (m^2/g, dry)	Pore size (nm)	Pore volume (mL/g)
DIAION CR10 (Na^+ type)	0.1	100–110	0.04
DIAION CR11 (Na^+ type)	27	340	0.5
DIAION CR20 (Cl^- type)	39	690	0.8

16. The difference in the palladium particle size on the catalyst surface between 8% Pd/CR11 and 9% Pd/CR20 would be solely attributed to the palladium density, thus the more condensed palladium on the Pd/CR11 surface should form larger particles in comparison to Pd/CR20.
17. The retention of the epoxide could be achieved by the Pd/C(en)-catalyzed hydrogenation in THF, while the use of MeOH as the solvent led to the regioselective cleavage of the terminal epoxides to the corresponding secondary alcohols; see: reference 5e and the following reference. Sajiki, H.; Hattori, K.; Hirota, K. *Chem. Commun.* **1999**, 1041–1042.
18. A similar solvent effect has been used for the partial and selective hydrogenation of alkynes to the corresponding alkenes, catalyzed by polyethylene imine-supported palladium (Pd/PEI); see reference[8].
19. The difference in the swellability of the catalyst by solvent might affect the ring-opening reaction of epoxides, but any evidences were not obtained.