Pd black deposited on polypropylene sheet as a highly selective catalyst for hydrogenation of alkenes

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Abstract—A catalyst deposited on a polypropylene sheet having an activity of almost the same level as commercially available Pd black and capable of promoting hydrogenolysis-free hydrogenation was developed. © 2003 Elsevier Science Ltd. All rights reserved.

In general, a palladium catalyst used for catalytic reduction (Pd black, Pd–C) is powdery, and filtration is required after the reaction. Because the palladium reduction catalyst is flammable and has the danger of ignition due to discharge by friction when put into a reactor, in particular, the dry type Pd–C catalyst must be handled carefully regardless of the amount.

Though the hydrogenation reaction[1] and hydrogenolysis[2] are quite different reactions, it is difficult to differentiate between them because the reaction conditions are the same. While many reaction methods for selective hydrogenation without hydrogenolysis (hydrogenolysis-free hydrogenation) have been reported, a paper reporting a 'palladium catalyst', which has a hydrogenation selective activity based on the catalyst preparation process, is extremely rare.[3] We have developed a catalyst having a selectivity, which is deposited on a polypropylene sheet, that has solved many of the problems caused by a powdery-type palladium reduction catalyst.
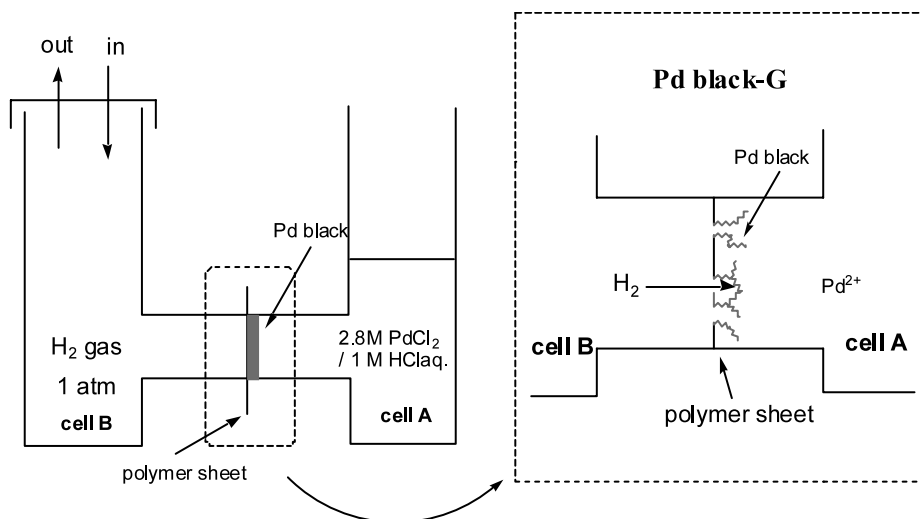

Figure 1.

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In our previous report,[4] we confirmed that a Pd black catalyst deposited on a palladium sheet exhibited the possibility of hydrogenolysis-free hydrogenation in benzene with good generality and exhibited excellent durability; the activity did not deteriorate after more than 1000 hours of reaction under actual reaction conditions. However, this catalyst has the general disadvantage in that the palladium sheet is expensive. Therefore, Pd black was deposited on an inexpensive gas permeable polypropylene sheet.[5]

A gas permeable polypropylene sheet (1 cm^2×1.0 mm) was placed between two cells (A and B), and a 28 mM PdCl$_2$/1 M HCl aqueous solution was poured into cell A, while the other cell B was filled with hydrogen gas at atmospheric pressure and room temperature. Pd black was deposited on the surface of the polymer sheet by reducing the palladium cation with hydrogen gas that passed through the sheet. The surface of the sheet was coated with Pd black (ca. 2 mg/cm^2) within 10 min (Fig. 1). The results of the reactions in various solvents[6] using benzyl ether 1[7] as the substrate and the Pd black catalyst deposited on a polypropylene sheet (Pd black-(G)) are shown in Table 1.

A general reaction method is as follows. A toluene solution (10 ml) of 1 (20 mg, 0.07 mmol) was added to a piece of Pd black-(G) (ca. 0.5 mg, 0.4 mg as a Pd black, 2% w/w) in a H$_2$ atmosphere at room temperature. After 4 h, the Pd black-(G) was simply removed from the reactant by forceps and the reactant was concentrated to give compound 2[8] in quantitative yield without any additional treatment.

When Pd black-(G) was used as the catalyst in benzene and toluene, a hydrogenolysis-free hydrogenation was clearly observed, and the compound 2 was obtained in quantitative yield as was done in the catalytic reaction using Pd black deposited on a palladium sheet.[4] No hydrogenolysis product 3[9] was obtained at all though the reaction was continued for a sufficient time in benzene and toluene after the reaction had been completed. In methanol,[10] 1 was immediately converted into 3, but 2 was not detected at all though the reaction products[6] were periodically analyzed during the reaction. In other solvents, though the selective hydrogenation was observed in some cases at about 4 h after starting the reaction, the hydrogenolysis also gradually proceeded.

Table 1. Solvent effect of hydrogenation reaction for benzyl ether 1
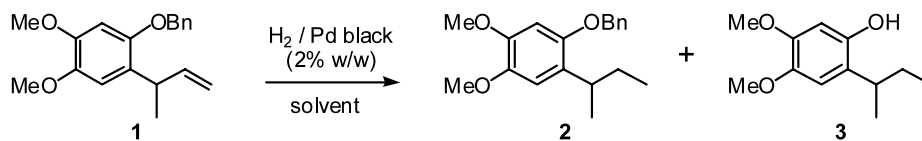
Solvent	Time (h)	2 (%)	3 (%)	1 (%)
Benzene*	4	100	0	0
	8	100	0	0
	24	100	0	0
Toluene*	4	100	0	0
	8	100	0	0
	24	100	0	0
Petroleum ether	4	100	~0	0
	8	100	~0	0
	24	85	15	0
1,4-Dioxane	4	79	21	0
1,2-Dimethoxy ethane	4	100	~0	0
	8	70	30	0
Isopropyl ether	4	100	0	0
	8	100	~0	0
	24	70	30	0
Ethyl acetate	4	81	19	0
Acetone	4	100	0	0
	8	100	~0	0
	24	91	9	0
Dichloromethane	4	100	~0	0
	8	93	7	0
Methanol*	4	0	100	0

* The reactions were completed in 1 h.

Table 2. Solvent effect of hydrogenation reaction for benzyl ester **4**
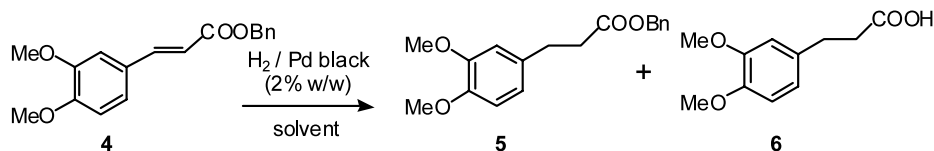
| Solvent	Time (h)	**5** (%)	**6** (%)	**4** (%)
Benzene*	4	100	0	0
	8	100	0	0
	24	100	0	0
Toluene*	4	100	0	0
	8	100	0	0
	24	100	0	0
Petroleum ether	4	43	0	57
	24	0	100	0
1,4-Dioxane	4	38	54	8
1,2-Dimethoxy ethane	4	65	29	6
Isopropyl ether	4	0	100	0
Ethyl acetate	4	21	79	0
Acetone	4	42	58	0
Dichloromethane	4	55	21	24
Methanol*	4	0	100	0

* The reactions were completed in 1 h.

The reactions in various solvents[6] were carried out for an alkene **4**[11] having a benzyl ester (Table 2). The clear hydrogenolysis-free hydrogenation was observed and **5**[12] was quantitatively obtained in benzene and toluene as was the case of the benzyl ether **1**. In methanol, **6**[13] was immediately formed; however, no formation of **5** was observed. Compounds **7** and **8**,[14] which were expected to be formed if the hydrogenolysis occurred, were not obtained from any of the reactions (Fig. 2).

In order to confirm the generality of the reaction of Pd black-(G) with functional groups, seven kinds of alkenes in addition to **1** and **4** were synthesized.[15] The reaction selectivity[6] was investigated using toluene as the solvent (Table 3).

The hydrogenolysis-free hydrogenation proceeded in an excellent manner for each substrate. Neither the hydrogenolysis product nor the decomposition product were observed though the reaction was con-tinued for a sufficient time after the reaction had been completed in order to verify the selectivity. It was confirmed that not only the hydrogenolysis of the benzyl group but also the hydrogenolysis of the allyl-oxy group was not promoted based on the results of entries 3 and 6.

In summary, though Pd black deposited on a palla-dium sheet[4] was able to promote the hydrogenolysis-free hydrogenation in benzene with good generality, it was not satisfactory because it has no hydrogenation selectivity in toluene, which was a substitute for ben-zene due to environmental and safety reasons. In con-trast, the Pd black-(G) having the reactivity[16] of existing Pd reduction catalysts exhibited a hydrogenolysis-free hydrogenation in toluene and has a high reactivity compared to the commercially avail-able Pd black[17], furthermore, it is not flammable. The Pd black-(G) excelled in durability, and no decline in activity and selectivity was observed after more than 1000 h[18] of reaction. Because the activity was stable even if the catalyst was left in the air, it also excels in storage capability as a reagent.
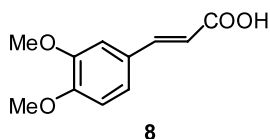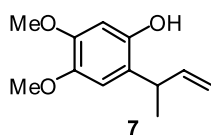
Acknowledgements

Figure 2.
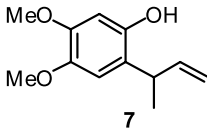
Table 3. Results of hydrogenation reaction for alkenes

Entry	Substrate	Product	Time (h)	Yield (%)	SM (%)
1*			4	100	0
			24	100	0
2			4	100	0
			24	100	0
3			4	100	0
			24	100	0
4			4	63	37
			8	100	0
			24	100	0
5			4	91	9
			8	100	0
			24	100	0
6*			4	100	0
			24	100	0
7*			4	100	0
			24	100	0
8			4	100	0
			24	100	0
9*			4	100	0
			24	100	0

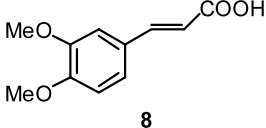Reaction conditions above arrow: Pd black-(G) (2% w/w), toluene, rt → Product + SM

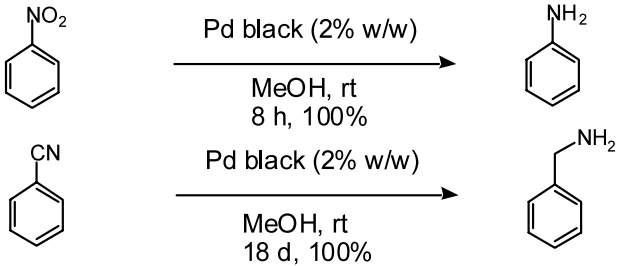* The reactions have been already completed in 1 hour.

References

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2. (a) Fletcher, H. G. *Methods Carbohydr. Chem.* **1963**, *II*, 166; (b) Bindra, J. S.; Grodski, A. *J. Org. Chem.* **1978**, *43*, 3240; (c) House, H. O. *Modern Synthetic Reactions*; W. A. Benjamin, Inc, 1972; pp. 23–26.
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4. Maki, S.; Harada, Y.; Hirano, T.; Niwa, H.; Yoshida, Y.; Ogata, S.; Nakamatsu, S.; Inoue, H.; Iwakura, C. *Synth. Commun.* **2000**, *30*, 3575–3583.

5. 3M Propore™ (Sumitomo 3M, Ltd). It is also good for the deposition and reaction to use Tyvek® (polyethylene).

6. After simply removing the Pd catalyst with forceps and concentrating the reaction solvent without carrying out any purification, the generation rate and the structure of all the reaction products were confirmed by directly measuring the residue using NMR and comparing this to the NMR data of the standard samples synthesized by alternative routes. Moreover, additional experiments were also carried out for all the reactions in order to confirm the reproducibility.

7. **1**: IR (neat) 1510, 1610, 1640 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.30 (3H, d, $J = 7.0$ Hz), 3.83 (6H, s), 3.90–4.00 (1H, m), 5.00–5.08 (2H, complex), 5.04 (2H, s), 5.96–6.09 (1H, m), 6.58 (1H, s), 6.71 (1H, s), 7.32–7.46 (5H, complex); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 19.59 (q), 35.20 (d), 56.12 (q), 56.56 (q), 71.80 (t), 99.84 (d), 111.58 (d), 112.82 (t), 126.33 (s), 127.33 (d), 127.82 (d), 128.50 (d), 137.46 (s), 142.94 (d), 143.48 (s), 147.58 (s), 149.79 (s); HRMS: found m/z 298.1573 (M$^+$); calcd for C$_{19}$H$_{22}$O$_3$ 298.1569.

8. **2**: IR (neat) 1505, 1610, 1630 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.83 (3H, t, $J = 7.6$ Hz), 1.18 (3H, d, $J = 6.9$ Hz), 1.51–1.63 (2H, complex), 3.13 (1H, tq, $J = 7.2$, 6.9 Hz), 3.83 (3H, s), 3.85 (3H, s), 5.02 (2H, s), 6.56 (1H, s), 6.72 (1H, s), 7.31–7.44 (5H, complex); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 12.18 (q), 20.87 (q), 30.14 (t), 33.21 (d), 55.98 (q), 56.53 (q), 71.74 (t), 98.81 (d), 110.94 (d), 127.18 (d), 127.65 (d), 128.30 (s), 128.38 (d), 137.55 (s), 143.47 (s), 147.08 (s), 150.12 (s); HRMS: found m/z 300.1728 (M$^+$); calcd for C$_{19}$H$_{24}$O$_3$ 300.1725.

9. **3**: IR (neat) 1590, 3450 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.87 (3H, t, $J = 7.5$ Hz), 1.22 (3H, d, $J = 6.6$ Hz), 1.60 (2H, quin, $J = 7.5$ Hz), 2.84 (1H, tq, $J = 7.5$, 6.6 Hz), 3.81 (3H, s), 3.83 (3H, s), 4.25 (1H, br. s, -OH), 6.41 (1H, s), 6.66 (1H, s); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 12.17 (q), 20.75 (q), 30.12 (t), 33.82 (d), 55.92 (q), 56.76 (q), 100.86 (d), 110.94 (d), 123.89 (s), 143.29 (d), 146.73 (s), 147.52 (s); HRMS: found m/z 210.1254 (M$^+$); calcd for C$_{12}$H$_{18}$O$_3$ 210.1256.

10. Other protonic solvents, for example EtOH and *i*-PrOH, gave results similar to those with MeOH.

11. **4**: IR (neat) 1505, 1595, 1615, 1700 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 3.90 (3H, s), 3.91 (3H, s), 5.25 (2H, s), 6.36 (1H, d, $J = 15.8$ Hz), 6.86 (1H, d, $J = 8.5$ Hz), 7.04 (1H, d, $J = 2.0$ Hz), 7.10 (1H, dd, $J = 8.5$, 2.0 Hz), 7.31–7.44 (5H, complex), 7.67 (1H, d, $J = 15.8$ Hz); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 55.83 (q), 55.93 (q), 66.22 (t), 109.54 (d), 110.98 (d), 115.51 (d), 122.67 (d), 127.30 (s), 128.19 (d), 128.24 (d), 128.56 (d), 136.13 (s), 145.05 (d), 149.17 (s), 151.14 (s), 166.98 (s); HRMS: found m/z 298.120 (M$^+$); calcd for C$_{18}$H$_{18}$O$_4$ 298.1205.

12. **5**: IR (neat) 1515, 1590, 1605, 1735 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 2.67 (2H, t, $J = 7.2$ Hz), 2.92 (2H, t, $J = 7.2$ Hz), 3.83 (3H, s), 3.85 (3H, s), 5.11 (2H, s), 6.70–6.79 (3H, complex), 7.28–7.39 (5H, complex); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 30.56 (t), 36.15 (t), 55.76 (q), 55.88 (q), 66.23 (t), 111.28 (d), 111.63 (d), 120.10 (d), 128.15 (d), 128.19 (d), 128.51 (d), 133.01 (s), 135.90 (s), 147.48 (s), 148.87 (s),

172.73 (s); HRMS: found m/z 300.1367 (M$^+$); calcd for C$_{18}$H$_{20}$O$_4$ 300.1362.

13. **6**: Mp 98–100°C; IR (neat) 1520, 1590, 1705, 3200 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 2.67 (2H, t, $J = 7.6$ Hz), 2.91 (2H, t, $J = 7.6$ Hz), 3.86 (3H, s), 3.87 (3H, s), 6.73–6.82 (3H, complex); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 30.24 (t), 35.79 (t), 55.81 (q), 55.91 (q), 111.35 (d), 111.66 (d), 120.08 (d), 132.76 (s), 147.58 (s), 148.92 (s), 178.54 (s); HRMS: found m/z 210.0896 (M$^+$); calcd for C$_{11}$H$_{14}$O$_4$ 210.0892.

14. Compounds **7** and **8** were synthesized by alternative routes, and the NMR data were compared with each reaction product.

7: IR (neat) 1590, 3450 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.37 (3H, d, $J = 6.9$ Hz), 3.63 (1H, dtq, $J = 6.9$, 5.9, 1.6 Hz), 3.79 (3H, s), 3.83 (3H, s), 5.16 (1H, dt, $J = 10.7$, 1.6 Hz), 5.17 (1H, dt, $J = 17.3$, 1.6 Hz), 5.23 (1H, br. s, -OH), 6.06 (1H, ddd, $J = 17.3$, 10.7, 5.9 Hz), 6.44 (1H, s), 6.65 (1H, s); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 12.17 (q), 20.75 (q), 30.12 (t), 33.82 (d), 55.92 (q), 56.76 (q), 100.86 (d), 110.94 (d), 123.89 (s), 143.29 (d), 146.73 (s), 147.52 (s); HRMS: found m/z 210.1254 (M$^+$); calcd for C$_{12}$H$_{18}$O$_3$ 210.1256.
8: Mp 178–180°C; IR (KBr) 1515, 1600, 1620, 1680, 3450 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$) δ 3.93 (6H, s), 6.33 (1H, d, $J = 15.8$ Hz), 6.88 (1H, d, $J = 8.2$ Hz), 7.08 (1H, d, $J = 1.7$ Hz), 7.14 (1H, dd, $J = 8.2$, 1.7 Hz), 7.73 (1H, d, $J = 15.8$ Hz); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 55.85 (q), 55.94 (q), 109.68 (d), 110.97 (d), 114.95 (d), 123.07 (d), 127.01 (s), 146.82 (d), 149.19 (s), 151.43 (s), 172.44 (s); HRMS: found m/z 208.0730 (M$^+$); calcd for C$_{11}$H$_{12}$O$_4$ 208.0736.

15. The structures of the synthesized compounds and the reaction products were determined based on various spectral data (IR, Mass, ^{1}H, ^{13}C NMR).

16. The reactivity of the Pd black-(G) in nitrobenzene and cyanobenzene was examined (Scheme). Nitrobenzene was satisfactorily reduced and quantitatively converted into aniline in 8 h in methanol under atmospheric pressure at room temperature. Cyanobenzene was reduced to the corresponding benzyl amine without producing a by-product though the reaction was very slow under atmospheric pressure and required 18 days to complete.

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18. It was confirmed that **1** was converted into **2** in quantitative yield within 1 h by employing Pd black-(G) which had been continuously used as a hydrogenation catalyst for 1000 h.