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Chemoselective Hydrogenation of Nitroarenes with Carbon Nanofiber-Supported Platinum and Palladium Nanoparticles

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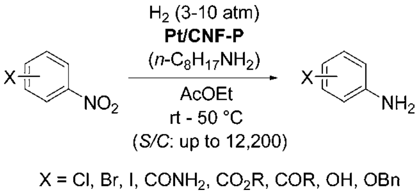
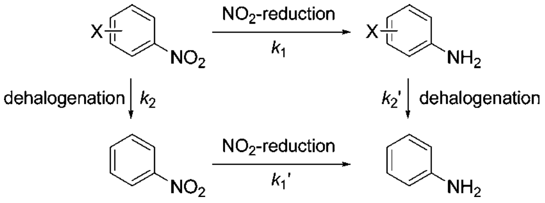
ABSTRACT



Platinum and palladium nanoparticles supported on three types of carbon nanofibers (CNFs) are synthesized and used as catalysts in the hydrogenation of nitroarenes. Nanosized platinum particles dispersed on platelet-type CNF efficiently catalyze the reduction of functionalized nitroarenes to the corresponding substituted anilines in high turnover numbers with other functional groups remaining intact.

Functionalized aniline derivatives are important intermediates in the preparation of dyes, herbicides, pesticides, and pharmaceuticals.[1] Catalytic hydrogenation of nitroarenes over heterogeneous catalysts is a simple method for the production of aromatic amines. However, the application of conventional catalytic systems to the reduction of nitroarenes containing other reducible functional groups, e.g., halogen, carbonyl, cyano, benzyloxy, and alkenic groups, is problematic because the reaction is often accompanied by the reduction of these functional groups.[2] A typical example is the preparation of haloanilines from halonitrobenzenes, where the hydrogenation over the conventional heterogeneous catalysts affords a mixture of haloaniline and dehalogenated aniline. This is due to the fact that reduction of a halogen atom (k_2 and k_2') competes with the reduction of a nitro group (k_1 and k_1'), as shown in Scheme 1.

Scheme 1. Reduction of Halonitrobenzene with Hydrogen



Although poisoning of the catalyst by sulfur-, nitrogen-, phosphorus-, or halogen-containing compounds sometimes suppresses the reductive dehalogenation,[2−4] the catalytic activity toward the reduction of the nitro group is also

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[1] Reviews: (a) Tafesh, A. M.; Weiguny, J. *Chem. Rev.* **1996**, *96*, 2035. (b) Downing, R. S.; Kunkeler, P. J.; van Bekkum, H. *Catal. Today* **1997**, *37*, 121. (c) Ono, N. *The Nitro Group in Organic Synthesis*; Wiley-VCH: New York, 2001. (d) Adams, J. P. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2586.

[2] (a) Rylander, P. In *Catalytic Hydrogenation in Organic Synthesis*; Academic Press: New York, 1979; p 112. (b) Baumeister, P.; Studer, M.; Roessler, F. In *Handbook of Heterogeneous Catalysis*; Ertl, G., Knözinger, H., Weitkamp, J., Eds.; Wiley-VCH: Weinheim, 1997; pp 2186−2209. (c) Blaser, H.-U.; Siegrist, U.; Steiner, H.; Studer, M. In *Fine Chemicals through Heterogeneous Catalysis*; Sheldon, R. A., van Bekkum, H., Eds.; Wiley-VCH: Weinheim, 2001; p 389.

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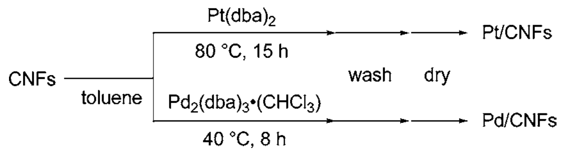
significantly decreased. Thus, the catalytic hydrogenation of *p*-chloro- and *p*-bromonitrobenzene using Pd and Pt/C−$ZnBr_2$ systems occurs below 65 °C under a hydrogen atmosphere (1 atm) to result in the exclusive formation of the corresponding haloanilines. However, the catalyst efficiency is low (substrate/catalyst mole ratio; $S/C = 100$ for Pd, and 20 for Pt).[3b] Use of sulfide-modified Co, Rh, Pd, and Pt/C as catalysts reportedly leads to high turnover numbers (TONs) [up to 2400 mol (substrate)/mol (metal)], but the reaction requires high temperatures and high H_2 pressures (100−175 °C, 30 atm) for a complete conversion to haloanilines.[3a] Thus, the development of a new catalyst system, which realizes an efficient conversion of halonitroarenes under mild conditions and provides a selective reduction of the nitro group with other functional groups remaining intact, is an important target in organic synthesis.

It is well known that the catalytic properties of heterogeneous catalysts are dependent on the particle size of the metal and the surface structure of the supports.[5] We have recently developed ruthenium nanoparticles supported on carbon nanofibers (CNFs) [CNFs are classified into three types, where graphite layers are either perpendicular (platelet: CNF−P), parallel (tubular: CNF−T), or stacked obliquely (herringbone: CNF−H)],[6] which showed a high efficiency in arene hydrogenation.[7] This is attributed to the high catalytic activity of nanosized ruthenium particles, which are effectively supported by nanolevel-controlled surface structures of CNF. We were interested in the application of nanometal particles supported on CNFs to the hydrogenation of nitroarenes in the hope that these may exhibit high catalytic activity with high selectivity toward the reduction of the nitro group. Attempted hydrogenation of halonitroarenes over Ru/CNFs led to problems in both the activity and the selectivity of the catalyst. However, Pt nanoparticles on CNFs (Pt/CNFs) were found to act as efficient hydrogenation catalysts for the conversion of nitroarenes to anilines in high TONs without affecting the reduction of halogen or other functional groups.

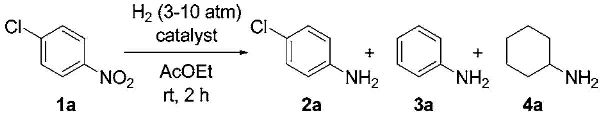
Preparation of Pt and Pd/CNFs was achieved successfully by the reaction of $Pt(dba)_2$ or $Pd_2(dba)_3{\cdot}CHCl_3$ with CNFs in toluene under an argon atmosphere (Scheme 2). Three types of CNF were used for the immobilization of platinum and palladium, where the metal particles could be highly dispersed on the surface in all cases with particle size range of 1−3 nm for Pt and 3−7 nm for Pd (see Supporting Information).

Scheme 2. Preparation of Pt and Pd/CNFs



The Pt and Pd/CNFs synthesized were used in the catalytic hydrogenation of *p*-chloronitrobenzene (**1a**). The reaction of **1a** (157 mg, 1 mmol) was carried out in the presence of the catalyst (5 mg; $S/C = 710{-}1630$) in ethyl acetate (3 mL) under H_2 pressure (initial pressure: $P_{H2} = 10$ atm) at room temperature (Table 1). The reaction over a commercially available Pt/C catalyst under similar conditions proceeded a turnover frequency (TOF: TON/h) of 650 to give a mixture of desired chloroaniline **2a** (75%), dechlorinated aniline **3a** (10%), and cyclohexylamine **4a** (12%). All of the Pt/CNFs used exhibited good to high catalytic efficiency in the reduction of the nitro group. **1a** was consumed within 2 h

Table 1. Hydrogenation of **1a** with Pt and Pd Catalysts



1a **2a** **3a** **4a**

entry	catalyst	solvent	**2a** (%)[a]	**3a** (%)[a]	**4a** (%)[a]	TOF
1	Pt/CNF−T	AcOEt	86	5	9	750
2	Pt/CNF−H	AcOEt	96	3	ND[b]	815
3	Pt/CNF−P	AcOEt	96.3[c]	3.7[c]	ND[b]	610
4	Pd/CNF−T	AcOEt	91.0[c]	9.0[c]	ND[b]	355
5	Pd/CNF−H	AcOEt	95.9[c]	4.1[c]	ND[b]	445
6	Pd/CNF−P	AcOEt	96.1[c]	3.9[c]	ND[b]	410
7	Pt/CNF−P	hexane	93	6	ND[b]	610
8	Pt/CNF−P	EtOH	86	7	7	610
9[d]	Pt/CNF−P	AcOEt	97.0[c]	1.5[c]	ND[b]	610
10[e]	Pt/CNF−H	AcOEt	97.1[c]	1.3[c]	ND[b]	815
11[e]	Pt/CNF−P	AcOEt	>99.9[c]	ND[b]	ND[b]	610
12[e,f]	Pd/CNF−P	AcOEt	>99.9[c]	ND[b]	ND[b]	165

[a] Determined by ^1H NMR analysis. [b] ND = not detected. [c] Determined by GLC analysis. [d] H_2 (3 atm). [e] 20 μL of *n*-octylamine (10 mol % to **1a**) was added. [f] For 5 h.

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(3) Representative papers: (a) Greenfield, H.; Dovell, F. S. *J. Org. Chem.* **1967**, *32*, 3670. (b) Baumeister, P.; Blaser, H. U.; Siegrist, U.; Studer, M. *Catal. Org. React.* **1998**, *75*, 207. (c) Wu, G.; Huang, M.; Richards, M.; Poirier, M.; Wen, X.; Draper, R. W. *Synthesis* **2003**, 1657. (d) Lee, H.-Y.; An, M. *Bull. Kor. Chem. Soc.* **2004**, *25*, 1717. (e) Akao, A.; Sato, K.; Nonoyama, N.; Mase, T.; Yasuda, N. *Tetrahedron Lett.* **2006**, *47*, 969. Other catalyst systems; Cp_2TiCl_2/Sm system: (f) Huang, Y.; Liao, P.; Zhang, Y.; Wang, Y. *Synth. Commun.* **1997**, *27*, 1059. Pt/C in $ScCO_2$: (g) Ichikawa, S.; Tada, M.; Iwasawa, Y.; Ikariya, T. *Chem. Commun.* **2005**, 924. Pt/C in ionic liquid: (h) Xu, D.-Q.; Hu, Z.-Y.; Li, W.-W.; Luo, S.-P.; Xu, Z.-Y. *J. Mol. Catal. A: Chem.* **2005**, *235*, 137. $Pd(OAc)_2$−hydrosilanes: (i) Rahaim, R. J., Jr.; Maleczka, R. E., Jr. *Org. Lett.* **2005**, *7*, 5087. $Mo(CO)_6$/DBU under microwave irradiation: (j) Spencer, J.; Anjum, N.; Patel, H.; Rathnam, R. P.; Verma, J. *Synlett* **2007**, 2557. Au/TiO_2: (k) Corma, A.; Serna, P. *Science* **2006**, *313*, 332, and references cited therein.

(4) Blaser, H.-U. *Science* **2006**, *313*, 312, and references cited therein.

(5) (a) Feldheim, D. L.; Foss, C. A., Jr. *Metal Nanoparticles: Synthesis, Characterization, and Application*; Marcel Dekker: New York, 2002. (b) *Catalyst Supports and Supported Catalysts*; Stiles, A. B., Ed.; Butterworths: Boston, 1987. (c) *Handbook of Heterogeneous Catalysis*; Ertl, G., Knözinger, H., Weitkamp, J., Eds.; VCH: Weinheim, 1997.

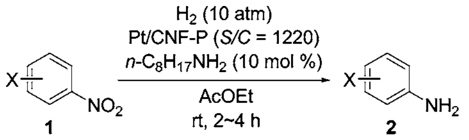
(6) The CNFs are classified into three types: graphite layers are perpendicular (platelet: CNF-P), parallel (tubular: CNF-T), and stacked obliquely (herringbone: CNF-H). These three CNFs can be synthesized selectively in large scales; see: (a) Rodriguez, N. M. *J. Mater. Res.* **1993**, *8*, 3233. (b) Tanaka, A.; Yoon, S.-H.; Mochida, I. *Carbon* **2004**, *42*, 591; 1291.

(7) (a) Motoyama, Y.; Takasaki, M.; Higashi, K.; Yoon, S.-H.; Mochida, I.; Nagashima, H. *Chem. Lett.* **2006**, *35*, 876. (b) Takasaki, M.; Motoyama, Y.; Higashi, K.; Yoon, S.-H.; Mochida, I.; Nagashima, H. *Chem. Asian J.* **2007**, *2*, 1524. (c) Takasaki, M.; Motoyama, Y.; Yoon, S.-H.; Mochida, I.; Nagashima, H. *J. Org. Chem.* **2007**, *72*, 10291.

and turnover frequencies reached 610−815 mol (**1a**)/mol (metal)•h (entries 1−3). The selectivity of the reduction of *p*-chloroaniline **2a** was highly dependent on the CNF support. The product ratio obtained in the reaction with Pt/CNF−T was similar to that of commercially available Pt/C in producing large amounts of **3a** and **4a** as byproducts (entry 1). In sharp contrast, the reaction over Pt/CNF−H and Pt/CNF−P improved the selectivity of **2a** up to 96%, in which the arene hydrogenation was suppressed effectively (entries 2 and 3). Pd/CNFs showed catalytic properties similar to the Pt/CNFs. The selectivity of the reaction of **2a** is about 96% when using Pd/CNF−H and Pd/CNF−P, but the activities of the catalysts are slightly lower (TOF = 355−445) than that found when using Pt/CNF−H or Pt/CNF−P (entries 4−6). The solvent strongly affects the chemoselectivity of the reaction, and a more selective formation of **2a** was attained in ethyl acetate than in hexane or EtOH (entries 3 vs 7 and 8). Lower H_2 pressure (3 atm) led to a higher selectivity toward **2a** (98.4%) as shown in entry 9. Complete suppression of the side reactions leading to **3a** and **4a** was achieved with Pt/CNF−P by adding *n*-octylamine (10 mol % for **1a**); *p*-chloroaniline **2a** was obtained as a single product in quantitative yield (entry 11). It is noteworthy that no retardation was observed on the addition of *n*-octylamine to the reaction when using the Pt/CNFs as catalysts. It is known that addition of heteroatom-containing compounds to the reaction medium in catalytic hydrogenation reactions often decreases the reaction rate. In fact, addition of *n*-octylamine to the reaction with the Pd/CNF−P catalyst, while resulting in exclusive formation of **2a**, led to a marked decrease of the reaction rate; TOF decreased from 410 to 165 [mol (**1a**)/mol (Pd)•h] (entries 6 vs 12).

Catalytic hydrogenation of other halogenated nitrobenzene derivatives (**1b**−**e**) were also achieved with high chemoselectivity when usig the Pt/CNF−P−*n*-octylamine system (Table 2). Both *ortho*- and *meta*-chloronitrobenzenes **1b** and **1c** were converted to the corresponding chloroanilines **2b** and **2c** in almost quantitative yields; only trace amounts of dechlorinated aniline **3a** were formed (entries 2 and 3). It is known that the hydrogenation of *p*-bromo- (**1d**) and *p*-iodonitrobenzene (**1e**) with high chemoselectivity is difficult to achieve with commercially available catalysts. In fact, we have found that Pt/C catalyst produced a 3:2 mixture of desired product **2d** (57%) and debrominated aniline **3a** (42%). Interestingly, the reaction with Pt/CNF−P under the same conditions afforded *p*-bromoaniline **2d** in 94% yield in the absence of an additive (entry 4), whereas addition of *n*-octylamine resulted in formation of **2d** in >99% yield with 99.8% selectivity (entry 5). Nitro-selective hydrogenation of *p*-iodonitrobenzene **1e** was also achieved with 97% selectivity by running the reaction with the Pt/CNF−P−amine system at 50 °C for 4 h (entry 6).

Table 2. Hydrogenation of Various Halogenated Nitroarenes **1a**−**e**[a]



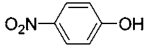
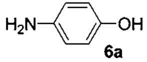
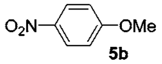
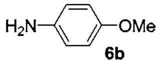
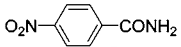
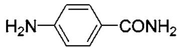
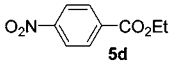
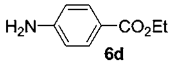
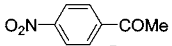
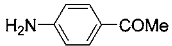
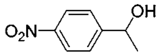
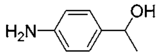
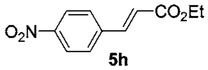
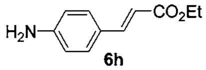
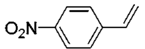
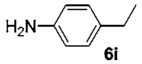
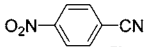
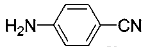
a: X = *p*-Cl
b: X = *m*-Cl
c: X = *o*-Cl
d: X = *p*-Br
e: X = *p*-I

entry	substrate	time (h)	**2** (%)[b]	**3** (%)[b]
1	**1a**	2	>99.9	ND[c]
2	**1b**	2	99.9	0.1
3	**1c**	4	98[d]	<2[d]
4[e]	**1d**	4	94[d]	6[d]
5	**1d**	4	99.7	0.2
6[f]	**1e**	4	96[d]	3[d]

[a] All reactions were carried out with **1** (1 mmol), Pt/CNF−P (5 mg), and *n*-octylamine (20 μL) in ethyl acetate at room temperature under H_2 (10 atm). [b] Determined by GLC analysis. [c] ND = not detected. [d] Determined by ^1H NMR analysis. [e] In the absence of *n*-octylamine. [f] At 50 °C.

Pt/CNF−P was also effective in the hydrogenation of other nitroarenes even in the absence of *n*-octylamine (Table 3).[8] Hydrogenation of *p*-nitrophenol (**5a**) gave *p*-aminophenol (**6a**) as a single product within 4 h. Aromatic hydrogenation leading to the corresponding cyclohexanone or cyclohexanol derivatives, which often seen in the hydrogenation with conventional heterogeneous catalysts, did not occur (entry 1). The nitro group was selectively reduced to the amino moiety with carbonyl groups present in the molecule remaining intact; no reduction of amide, ester, or ketone groups

Table 3. Hydrogenation of Other Nitroarenes **5a**−**h**[a]

entry	substrate	product	Yield (%)
1	 **5a**	 **6a**	>99
2	 **5b**	 **6b**	>99
3[b]	 **5c**	 **6c**	96
4[c]	 **5d**	 **6d**	99
5	 **5e**	 **6e**	98
6	 **5f**	 **6f**	>99
7	 **5g**	 **6g**	82[de]
8	 **5h**	 **6h**	91[df]
9	 **5i**	 **6i**	>99
10	 **5j**	 **6j**	64[dg]

[a] All reactions were carried out with **5** (1 mmol) and Pt/CNF−P (5 mg; *S*/*C* = 1220) in ethyl acetate (3 mL) at rt for 4 h under H_2 (10 atm). [b] In THF/EtOH = 2:1 at 100 °C for 12 h under 25 atm of H_2. [c] 5 mmol of **5d** (*S*/*C* = 6100) and 15 mL of solvent were used. [d] Determined by ^1H NMR analysis. [e] 18% of substrate **5g** was recovered. [f] 9% of ethyl *p*-aminodihydrocinnamate **7** was formed. [g] 32% of di(*p*-aminobenzyl)amine was formed.

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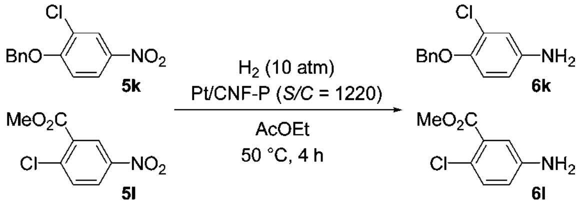
(8) No reduction took place in the reaction of aliphatic nitro compounds.

was observed as shown in entries 3−5. Although the catalytic hydrogenation over heterogeneous catalysts often induces hydrogenolytic cleavage of the C−O bond in benzyl alcohols or benzyl ethers, nitroarenes containing the benzyloxy group (**5f**) or the benzyl alcohol moiety (**5g**) were completely converted to the corresponding aniline derivatives **6f** and **6g** without cleavage of the benzyl group (entries 6 and 7). Reduction of the nitro group was favored with ethyl *m*-nitrocinnamate (**5h**) affording ethyl *m*-aminocinnamate (**6h**) with 91% selectivity (entry 8). In the reaction of *p*-nitrostyrene (**5i**), however, nitro- and alkenyl groups were both reduced by the present system to afford *p*-ethylaniline (**6i**) as a single product in quantitative yield (entry 9). Attempted nitro-selective reduction of *p*-cyanonitrobenzene (**5j**) gave the desired *p*-cyanoaniline (**6j**) in 64% yield along with 32% of di(*p*-aminobenzyl)amine (entry 10). We also examine the reaction of 3-nitropyridine as a nitro-substituted heteroarene. However, the desired 3-aminopyridine was formed in only 13% yield; the main product was the intermediary hydroxyl amine derivative.

The results shown in Tables 2 and 3 suggest that the hydrogenation of nitroarenes over Pt/CNF−P is tolerant toward halogen and other functional groups. This is clearly demonstrated by the selective hydrogenation of the nitro group in trisubstituted benzene derivatives (**5k** and **5l**) over the Pt/CNF−P catalyst. In these cases, nitro-selective reduction proceeded without addition of *n*-octylamine to give 3-chloro-4-benzyloxyaniline (**6k**) and 3-carbomethoxy-4-chloroaniline (**6l**), respectively, as a single product in quantitative yields (Scheme 3).

Scheme 3. Nitro-selective Reduction of Trisubstituted Benzene Derivatives **5k** and **5l**



Above-described results clearly demonstrate that Pt/CNF−P is an effective catalyst for selective hydrogenation of the nitro group in various nitroarenes with other functional groups remaining intact. In the hydrogenation of halonitroarenes, addition of *n*-octylamine contributes to raising the selectivity without retarding the reduction of the nitro group. Besides the efficiency and selectivity in the reaction, the hydrogenation over Pt/CNF−P has two more advantages; reusability without leaching of platinum species and possible application to production of anilines in gram quantities, which is exemplified by the following experiments: (1) after the reaction with **5b** (Table 3, entry 2), the catalyst was recovered by filtration and reused in the same reaction. *p*-Methoxyaniline **6b** was obtained in a yield of over 99% with repeated use of the catalyst (5×). No Pt species was detected in the product (<30 ppb, determined by ICP−MS). (2) The hydrogenation of **5b** (1.53 g, 10 mmol) over Pt/CNF−P (5 mg, 3.2 wt %; 160 μg of Pt) at room temperature for 4 h under H_2 (10 atm) afforded **6b** in quantitative yield (1.23 g). The TON of the reaction was calculated to be 12 200 (TOF = 3050/h).

In conclusion, we have developed a catalytic system consisting of nanoplatinum particles dispersed on nanocarbon fiber support, Pt/CNF−P. Pt/CNF−P has been found to be an efficient and reusable catalyst for the hydrogenation of nitroarenes to aromatic amines. The reaction proceeds under mild conditions in high TONs with other functional groups remaining intact. Since the average particle size of the Pt is independent of the type of CNF, we consider that the high chemoselectivity seen in the nitro-group selective hydrogenation of halonitrobenzenes accompanied by efficient catalyst poisoning by *n*-octylamine with Pt/CNF−P are rather attributed to the steric and/or electronic effects derived from interaction between Pt particles and the CNF support than the size of platinum particles. A detailed mechanistic study is now under investigation.

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Supporting Information Available: Experimental procedures and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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