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Chemoselective Hydrogenation of Functionalized Nitroarenes and Imines by Using Carbon Nanofiber-Supported Iridium Nanoparticles

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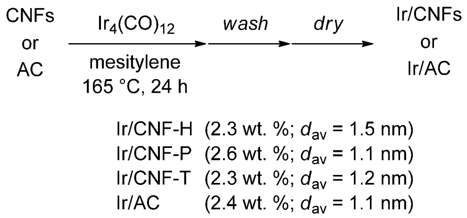
Abstract: The reaction of three types of carbon nanofibers (CNFs; platelet: CNF-P, tubular: CNF-T, herringbone: CNF-H) with $Ir_4(CO)_{12}$ in mesitylene at 165 °C provided the corresponding CNF-supported iridium nanoparticles, Ir/CNFs (Ir content = 2.3–2.6 wt. %). Transmission electron microscopy (TEM) studies of these Ir/CNF samples revealed that size-controlled Ir nanoparticles (average particle size of 1.1–1.5 nm) existed on the CNFs. Among the three Ir/CNF samples, Ir/CNF-T showed an excellent catalytic activity and chemoselectivity towards hydrogenation of functionalized nitroarenes and imines; the corresponding aniline derivatives were obtained with high turnover numbers at ambient temperature under 10 atm of H_2, and the catalyst is reusable. Ir/CNF-T was also effective for the reductive *N*-alkylation of anilines with carbonyl compounds.

Recently, much attention has been paid to the development of transition metal nanoparticles for technological applications in various areas such as chemical sensors, electrocatalysts for fuel cells, and heterogeneous catalysts for organic transformations.[1] Although a number of solid-supported transition metal nanoparticles (NPs), such as Ru, Rh, Ni, Pd, and Pt NPs, have been widely used as heterogeneous catalysts for various organic transformations,[1,2] the use of supported iridium catalysts is limited to the hydrogenation of alkenes, arenes, and nitro compounds.[3] Since the catalytic properties of these heterogeneous catalysts are highly dependent on the surface design of the support along with the size and shape of the metal nanoparticles,[1,2] the search for more suitable solid supports for iridium nanoparticles to provide highly active and selective catalysts is a challenging problem.

In this context, carbon nanofibers (CNFs) that have controlled nanostructures consisting of stacked graphene sheets are attractive supports for metal nanoparticles. 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) to the fiber axis.[4] We have recently established selective synthetic methods for the preparation of carbon nanofibers (CNFs)[4c,d] and explored methods to immobilize ruthenium, rhodium, palladium, and platinum nanoparticles on their surface by thermal decomposition of organometallic precursors.[5] The Ru, Rh, Pd, and Pt/CNFs thus produced act as efficient catalysts for arene hydrogenation (Ru- and Rh/CNFs)[5a,b,d,e] and the reduction of aromatic nitro compounds (Pd- and Pt/CNFs)[5c,f] with high turnover numbers. It is important that neither sintering nor leaching of metal nanoparticles is observed after the reaction; this results in possible reuse of the catalyst without loss of the catalytic activity. In this paper, we report that iridium nanoparticles can be immobilized on the surface of CNFs by a procedure similar to that used for Ru- and Rh/CNFs (see Scheme 1), which are prepared by pyrolysis of metal carbonyl clusters, and that the resulting Ir nanoparticles (see Figure S1 in the Supporting Information for TEM images of the obtained samples and their size distribution), Ir/CNF-P and Ir/CNF-T, behave as an efficient catalyst for nitro- and imino-selective hydrogenation of functionalized nitroarenes and imines.



Scheme 1. Preparation of Ir/CNFs and Ir/AC.

The catalytic activity of Ir/CNFs is compared with that of iridium nanoparticles supported on activated carbon (Ir/AC) using various organic compounds as substrate. The reaction was carried out using 1 mL of substrate and 5 mg of Ir cata-

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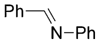
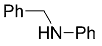
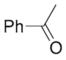
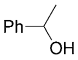
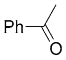
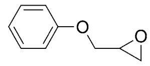
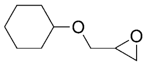
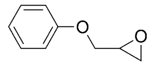
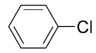
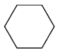
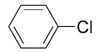
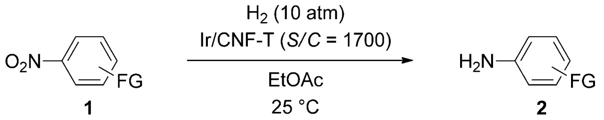
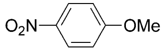
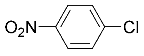
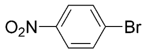
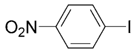
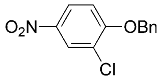
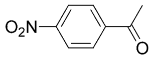
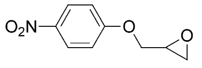
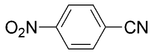
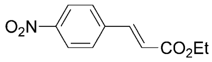
Table 1. Hydrogenation of various substrates using Ir/CNFs and Ir/AC as a catalyst.[a]

Entry	Substrate	Catalyst	Product	TOF[b]
1	$Ph{-}NO_2$	Ir/AC	$Ph{-}NH_2$	65
2	$Ph{-}NO_2$	Ir/CNF-H	$Ph{-}NH_2$	82
3	$Ph{-}NO_2$	Ir/CNF-P	$Ph{-}NH_2$	180
4	$Ph{-}NO_2$	Ir/CNF-T	$Ph{-}NH_2$	150
5[c]		Ir/CNF-T		160
6		Ir/CNF-T		130
7[d]		Ir/CNF-T	no reaction	–
8		Ir/CNF-T		30
9		Ir/CNF-P	no reaction	–
10		Ir/CNF-T		20
11[d]		Ir/CNF-T	no reaction	–
12	Ph–CN	Ir/CNF-T	no reaction	–

[a] Unless stated otherwise, all reactions were performed using substrate (1 mL) and Ir catalyst (5 mg) at 25 °C for 12 h under H_2 (initial pressure = 10 atm). [b] TOF = mol (product)/mol (Ir)·h. [c] 9 mmol of imine and 3 mL of ethyl acetate was used. [d] 5 mol % of Et_3N was added.

Table 2. Hydrogenation of various nitroarenes **1a–i** to anilines **2a–i** using Ir/CNF-T as a catalyst.[a]



Entry	Substrate	t [h]	Product	Yield [%]
1		60	**2a**	98
2		11	**2b**	99
3		11	**2c**	99
4[b,c]		17	**2d**	99
5[b]		11	**2e**	98
6		11	**2f**	97
7[c]		36	**2g**	99
8[b,c]		30	**2h**	92[d]
9		53	**2i**	83[e]

[a] Unless stated otherwise, all reactions were performed using **1** (1 mmol) and Ir/CNF-T catalyst [*S/C* = 1700 mol (**1**)/mol (Ir)] in ethyl acetate (3 mL) at 25 °C under H_2 (initial pressure = 10 atm). [b] At 50 °C. [c] *S/C* = 500 mol (**1**)/mol (Ir). [d] 3 % of di(4-aminobenzyl)amine was formed. [e] 16 % of ethyl 4-aminodihydrocinnamate was formed.

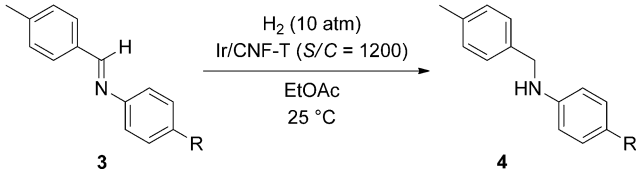
lyst for 12 h at 25 °C under H_2 (10 atm), except in the case of a solid substrate, *N*-phenylbenzaldimine. As shown in Table 1, entries 1–4, all iridium nanoparticles acted as catalysts for the hydrogenation of nitrobenzene, and Ir/CNF-P and Ir/CNF-T showed good catalytic activity;[6] the turnover frequency (TOF) of the reaction over these catalysts were 180 [mol (product)/mol (Ir)·h] for Ir/CNF-P and 150 for Ir/CNF-T, respectively (entries 3 and 4). Ir/CNF-T also acted as a good catalyst for the reduction of imines and ketones; the hydrogenation of *N*-phenylbenzaldimine and acetophenone over Ir/CNF-T proceeded with TOFs of 160 and 130 to afford *N*-phenylbenzylamine and 1-phenyl ethanol, respectively, as the sole product (entries 5 and 6). Phenyl glycidyl ether was converted into cyclohexyl glycidyl ether (TOF = 30) through arene hydrogenation, without promoting the ring-opening hydrogenation of the epoxide group; however, no reaction proceeded using Ir/CNF-P as a catalyst (entry 8 vs. entry 9). The reaction of chlorobenzene gave cyclohexane (TOF = 20), which was obtained by hydrogenolytic cleavage of the C–Cl bond of chlorobenzene followed by arene hydrogenation (entry 10). By contrast, in the case of nitrile compounds, no reaction took place and the starting material was recovered quantitatively (entry 12). It is noteworthy that the addition of a small amount of amine to the reaction mixture eliminated the catalytic activity of Ir/CNF-T towards the reduction of the keto group, hydrogenolytic cleavage of the C–Cl bond, and hydrogenation of the aromatic ring (entries 7 and 10).[7]

The usefulness of Ir/CNF-T was demonstrated by the hydrogenation of nitroarenes that contain other reducible functional groups (Table 2). It is well known that the hydrogenation of halogenated nitrobenzenes over conventional heterogeneous catalysts affords a mixture of aniline and halogenated aniline; therefore, sulfur-, nitrogen-, phosphorus-, or halogen-containing compounds are often added as a catalyst poison to improve the chemoselectivity.[5d,f,8] We previously reported that the hydrogenation of 4-chloro- and 4-bromonitrobenzene (**1b** and **1c**, respectively) over Pd- and Pt/CNF produced aniline in 4–6 % yield.[5d] However, complete suppression of the reductive dehalogenation was achieved in the reaction of halonitrobenzenes over Ir/CNF-T under H_2 (initial pressure = 10 atm); 4-chloro-, 4-bromo-, and 4-iodonitrobenzene (**1b–d**) were converted into the corresponding halogenated anilines **2b–d** in almost quantitative yields without contamination by the dehalogenated aniline (entries 2–4). Furthermore, the nitro group was selectively reduced to the amino moiety in the presence of benzyloxy and carbonyl groups; the reduction of the keto group and the hydrogenolytic cleavage of the C–O bond in the benzyloxy group, which are often seen in the Pd/C-catalyzed hydrogenation, were not observed (entries 5 and 6). It is also well known that the nitro-selective reduction of nitro compounds bearing an epoxide group is difficult to achieve because the ring-opening reaction of the highly strained epoxy function proceeds easily under reductive conditions.[9] In fact, Sajiki and co-workers reported that the reaction of (nitrophenyl)methyl glycidyl ethers over Pd/C(en) catalyst afforded a mixture of (aminophenyl)methyl glycidyl ethers and its ring-opening products (93–95 % selectivity).[10] However, in our study (4-aminophenyl)methyl glycidyl ether (**2g**) was obtained as the sole product in the reaction with an increased amount of catalyst (substrate/catalyst molar ratio *S/C* = 500, entry 7).[11] Reduction of the nitro group was favored with 4-cyanonitrobenzene (**1h**), affording 4-cyanoaniline (**2h**) in 92 % yield, but small amounts of di(4-aminobenzyl)amine, which forms by reductive alkylation via eliminating NH_3,[12,13] and other unidentified compounds were obtained as by-products (entry 8). The attempted nitro-selective reduction of ethyl 4-nitrocinnamate (**1i**) gave the desired ethyl 4-aminocinnamate (**2i**) in 83 % yield along with 16 % of ethyl 4-aminodihydrocinnamate (entry 9).

Ir/CNF-T could be reused without loss of catalyt performance. After the hydrogenation of 4-chloronitrobenzene (**1b**) (*S/C* = 2300) was performed in ethyl acetate at 25 °C for 12 h under H_2 (initial pressure = 10 atm), the catalyst was recovered by filtration and subjected to subsequent hydrogenation reactions. Even after the fifth run, **1b** was completely consumed and 4-chloroaniline (**2b**) was obtained as the sole product in 99 % yield.

Ir/CNF-T is also a useful catalyst for the chemoselective reduction of functionalized imines to the corresponding amines (Table 3). Similar to the reduction of halogenated nitrobenzenes, imines having aromatic carbon–halogen bonds (**3b**: R = Cl, **3c**: R = Br) were converted into the corresponding secondary amines **4b** and **4c** in quantitative yields without contamination by the dehalogenated aniline derivative (entries 2 and 3). Furthermore, the imino group was selectively reduced to the amino moiety in the reaction of *N*-(4-acetylphenyl)-4-methylbenzaldimine (**3d**); the reduction of the keto group did not proceed and the amino ketone **4d** was obtained in quantitative yield (entry 4).

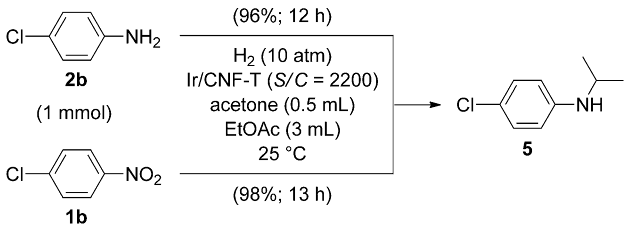
Table 3. Hydrogenation of imines **3a–d** using Ir/CNF-T as a catalyst.[a]



Entry	Substrate	*t* [h]	Product	Yield [%]
1	**3a:** R = H	12	**4a**	99
2	**3b:** R = Cl	12	**4b**	99
3	**3c:** R = Br	12	**4c**	99
4	**3d:** R = COMe	21	**4d**	99

[a] All reactions were performed using **3** (1 mmol) and Ir/CNF-T catalyst [*S/C* = 1200 mol (**3**)/mol (Ir)] in ethyl acetate (3 mL) at 25 °C under H_2 (initial pressure = 10 atm).

The above described results clearly demonstrate the high chemoselectivity, efficiency, and reusability of the Ir/CNF-T catalyst in the hydrogenation of functionalized nitroarenes and imines to the corresponding amines. Another application of Ir/CNF-T as a hydrogenation catalyst is the reductive *N*-alkylation of anilines with carbonyl compounds (Scheme 2).[14] For example, the reaction of 4-chloroaniline (**2b**) with acetone in ethyl acetate in the presence of Ir/CNF-T (*S/C* = 2200) at 25 °C for 12 h under H_2 (initial pressure = 10 atm) afforded *N*-isopropyl-4-chloroaniline (**5**) in 96 % yield. Furthermore, direct and one-pot reductive *N*-alkylation can be achieved by using nitrobenzenes as an amine source; 4-chloronitrobenzene (**1b**) was treated with acetone in the presence of Ir/CNF-T (*S/C* = 2200) at 25 °C for 13 h under H_2 (initial pressure = 10 atm) to afford *N*-isopropyl-4-chloroaniline (**5**) in 98 % yield. In both cases, reductive dechlorination did not proceed and the alkylated product **5** was obtained as the sole product.



Scheme 2. Reductive *N*-alkylation of 4-chloroaniline (**2b**) and 4-chloronitrobenzene (**1b**) with acetone over Ir/CNF-T under H_2 (10 atm).

In conclusion, we have successfully synthesized iridium nanoparticles supported on carbon nanofibers (Ir/CNFs) and activated carbon (Ir/AC) with a narrow size distribution by thermal decomposition of $Ir_4(CO)_{12}$ in the presence of the carbon supports. Among them, Ir/CNF-T has been found to be an efficient catalyst for the hydrogenation of nitroarenes and imines to the corresponding aniline derivatives. These reactions proceed under mild conditions with high TONs with other functional groups remaining intact. Since the average size of the Ir particles is independent of the type of CNFs, we consider that the catalytic activity seen in the hydrogenation reactions can be mainly attributed to steric and/or electronic effects derived from interactions between Ir nanoparticles and the CNF support rather than the size of iridium particles. A detailed mechanistic study is now under investigation.

Experimental Section

Preparation of Ir/CNF-T

To a suspension of CNF-T (100 mg) in mesitylene (17 mL) was added $Ir_4(CO)_{12}$ (7.2 mg, [Ir] = 5.0 mg) under an argon atmosphere. After stirring at 165 °C for 24 h, the insoluble carbon materials were isolated by filtration using membrane filters (Durapore; 0.45 μm HV). The solids were washed with toluene (50 mL) and ether (50 mL) and then dried under vacuum (0.04 Torr) at room temperature for 3 h to afford Ir/CNF-T. To prevent oxidation of Ir species from air, Ir/CNF-T was stored under an inert atmosphere.

Hydrogenation of Nitroarenes

The hydrogenation of nitroarenes was performed in a 100 mL stainless steel autoclave fitted with a glass inner tube in the presence of nitroarene (**1**, 1 mmol), ethyl acetate (3 mL), and Ir/CNF-T [*S/C* = 1700 or 500 mol (**1**)/mol (Ir)] at 25 or 50 °C under H_2 (initial pressure = 10 atm). After completion of the reaction, the insoluble catalyst was removed by filtration, and the filtrate was concentrated under reduced pressure to give aniline **2** as the product. The purity of the product was determined by capillary gas–liquid chromatography (GLC) and/or ^{1}H NMR spectroscopic analysis.

Hydrogenation of Imines

The hydrogenation of imines was performed in a 100 mL stainless steel autoclave fitted with a glass inner tube in the presence of nitroarene (**3**, 1 mmol), ethyl acetate (3 mL), and Ir/CNF-T [$S/C=1200$ mol (**3**)/mol (Ir)] at 25 °C under H_2 (initial pressure = 10 atm). After completion of the reaction, the insoluble catalyst was removed by filtration, and the filtrate was concentrated under reduced pressure to give amine **4** as the product. The purity of the product was determined by capillary GLC and/or ^{1}H NMR spectroscopic analysis.

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Keywords: carbon nanofibers · heterogeneous catalysis · hydrogenation · imines · nitroarenes

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[6] The catalytic activity of Ir/CNF-T decreased remarkably at an H_2 pressure below 5 atm, and the hydroxylamine derivative, which is the intermediary species in the hydrogenation of nitrobenzene to aniline, was obtained as the major product.

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