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Rhodium Nanoparticles Supported on Carbon Nanofibers as an Arene Hydrogenation Catalyst Highly Tolerant to a Coexisting Epoxido Group

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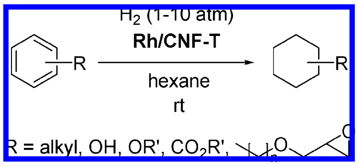
ABSTRACT



Rhodium nanoparticles supported on a carbon nanofiber (Rh/CNF-T) show high catalytic activity toward arene hydrogenation under mild conditions in high turnover numbers without leaching the Rh species; the reaction is highly tolerant to epoxido groups, which often undergo ring-opening hydrogenation with conventional catalysts.

Arene hydrogenation over heterogeneous catalysts has taken part in the facile production of substituted cyclohexane derivatives on both laboratory and industrial scales.[1] Among various transition metal catalysts, rhodium supported on activated carbons (Rh/C) generally shows higher catalytic activity for arene hydrogenation than heterogeneous catalysts containing other transition metals.[1c] However, one drawback to the use of expensive rhodium is that the catalyst is often quickly deactivated due to facile sintering of the metal particles and leaching of metallic species from the support, making the use of recycled Rh/C difficult.[2] Since catalytic properties of heterogeneous catalysts are highly dependent on the surface design of the support,[3] a search for carbon materials that promote arene hydrogenation under mild conditions with high turnover frequency and are robust enough to be reusable may provide a more suitable support for the rhodium catalysts. In this context, carbon nanofibers (CNFs) having controlled nanostructures consisting of stacked graphene sheets are attractive supports for metal particles. 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 these CNFs[4b,c] and explored methods to immobilize ruthenium, palladium, and platinum nanoparticles on their surface by decomposition of organometallic precur-

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(1) Reviews: (a) Weissernicl, K.; Arpe, H. J. *Industrial Organic Chemistry*, 2nd ed.; VCH: New York, 1993; p 343. (b) Stanislaus, A.; Cooper, B. H. *Catal. Rev. Sci. Eng.* **1994**, *36*, 75. (c) Augustine, R. L. *Heterogeneous Catalysis for the Synthetic Chemist*; Marcel Dekker: New York, 1996; Chapter 17. (d) Harman, W. D. *Chem. Rev.* **1997**, *97*, 1953. (e) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *191*, 187. (f) Dyson, P. J. *Dalton Trans* 2003, *2964*.

(2) Halttunen, M. E.; Niemelä., M. K.; Krause, A. O. I.; Vuori, A. I. *J. Mol. Catal. A: Chem.* **1996**, *109*, 209.

(3) (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.

(4) (a) Rodriguez, N. M. *J. Mater. Res.* **1993**, *8*, 3233. These three CNFs can be synthesized selectively in large scales; see: (b) Tanaka, A.; Yoon, S.-H.; Mochida, I. *Carbon* **2004**, *42*, 591. (c) Tanaka, A.; Yoon, S.-H.; Mochida, I. *Carbon* **2004**, *42*, 1291.

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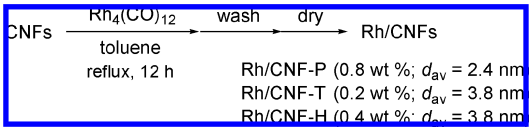
sors.[5] The Ru, Pd, and Pt/CNFs thus produced act as efficient catalysts for arene hydrogenation and the reduction of nitro compounds in high turnover numbers. It is important that neither sintering nor leaching of metallic species is observed; this results in possible reuse of the catalyst without loss of the activity. In this paper, we wish to report that rhodium nanoparticles can be immobilized on the surface of the three types of CNFs by a procedure similar to that used for Ru/CNF and that one of the resulting Rh/CNFs, Rh/CNF-T, behaves as a highly efficient reusable catalyst for arene hydrogenation under mild conditions.[6] Of particular interest is that the use of Rh/CNF-T allows the hydrogenation of aromatic compounds having glycidyl moiety without promoting the ring-opening hydrogenation of the epoxido group.

Scheme 1 shows a synthetic procedure of the CNF-supported rhodium nanoparticles (Rh/CNFs). Thermal decomposition of $Rh_4(CO)_{12}$ (3.0 mg; [Rh] = 1.65 wt % for the support) in the presence of three types of carbon nanofibers (100 mg) in refluxing toluene under an argon atmosphere followed by filtration and washing with toluene and ether afforded the corresponding Rh/CNF-P, Rh/CNF-H, and Rh/CNF-T. The formation of rhodium nanoparticles on the CNFs was confirmed by transmission electron microscopy (TEM), and these nanoparticles were dispersed on the surface in all CNFs with an average particle size of 2.4 nm for Rh/CNF-P and 3.8 nm for both Rh/CNF-T and Rh/CNF-H, respectively (see Supporting Information). The rhodium content of the Rh/CNFs was determined by inductively coupled plasma-mass (ICP-MS) analysis; 0.8 wt % for Rh/CNF-P, 0.2 wt % for Rh/CNF-T, and 0.4 wt % for Rh/CNF-H, respectively.

Scheme 1. Preparation of Rh/CNFs



The catalytic activity of Rh/CNFs is compared with those reported in the literature using benzene as a simple and standard substrate.[7,8] To our knowledge, the most active arene hydrogenation catalyst in the literature was reported by Park and co-workers: rhodium nanoparticles entrapped in boehmite matrix, Rh/AlO(OH).[7] The turnover frequency (TOF) of the benzene hydrogenation over Rh/AlO(OH) catalyst was 200 [mol (benzene)/mol (Rh)•h] at 22 °C under 1 atm of H_2.[9] Hydrogenation of benzene (1 mmol) in the presence of the Rh/CNFs (5 mg) was carried out in hexane (1 mL) at room temperature under a hydrogen atmosphere. After 3 h, the conversion was determined by GC, from which the TOF was calculated. The results are summarized in Table 1. The TOF was dependent on the CNF; the reaction smoothly proceeded with both Rh/CNF-P and Rh/CNF-T, whereas no reaction took place using Rh/CNF-H as the catalyst. In particular, Rh/CNF-T showed high catalytic efficiency, and the TOF of the reaction reached over 1,000 [mol (benzene)/mol (Rh)•h] (entries 1−3). The TOF of the solventless hydrogenation at 75 °C under H_2 pressure (initial pressure: $P_{H_2} = 4$ atm) reached 7,750 (entry 4). These TOFs have catalytic efficiencies 5 times higher than those of Park's Rh/AlO(OH) catalyst at ambient temperature under 1 atm of H_2 (entry 5) and at 75 °C under 4 atm of H_2 (entry 6). As previously stated, the hydrogenation of benzene is efficiently catalyzed by Ru/CNFs; however, the reactions required application of slightly higher temperature (>40 °C) and hydrogen pressure (>10 atm). The activity of Ru/CNFs was dependent on the CNF used; the order of activity for the hydrogenation was Ru/CNF-P > Ru/CNF-H ≫ Ru/CNF-T,[5b] different from Rh/CNF-T > Rh/CNF-P ≫ Rh/CNF-H. In the experiments shown in entries 1 and 3, the catalyst was recovered and subjected to repeated experiments for hydrogenation of benzene (5 times). Neither loss of catalytic activity nor leaching of the metallic species was observed.

Table 1. Hydrogenation of Benzene with Rh Catalysts[a]

entry	catalyst	S/C[b]	P_{H_2} (atm)	temp (°C)	TOF[c]
1	Rh/CNF-P	2,500	1	rt	120
2	Rh/CNF-H	5,100	1	rt	*d*
3	Rh/CNF-T	10,300	1	rt	1,060
4[e]	Rh/CNF-T	116,000	4	75	7,750
5	Rh/AlO(OH)[f]	100	1	22	200
6[e]	Rh/AlO(OH)[f]	10,000	4	75	1,250

[a] All reactions were carried out with benzene (1 mmol) and Rh/CNF catalyst (5 mg) in hexane (1 mL) at room temperature. [b] S/C = mol (benzene)/mol (Rh). [c] TOF = mol (product)/mol (Rh)•h. The product yield was determined by GLC analysis. [d] The product was not detected. [e] 1 mL of benzene and no solvent was used. [f] Reference 7.

Phenol is a good substrate for investigating the performance of the catalyst in the selectivity. It is known that cyclohexanol (**1**) is a final product in the hydrogenation; however, incomplete hydrogenation results in the formation of intermediary cyclohexen-1-ol (**3**), which is isolated as cyclohexanone (**2**). Three commercially available Rh/C catalysts were subjected to hydrogenation of phenol at room temperature under 3 atm of H_2. In all cases, the catalyst was recycled and used for a second run under the same conditions. One of them showed no activity (entry 5) in both the first and second run, whereas one of the others exhibited low activity (TOF = ca. 11) to give a 3:7−2:8 mixture of **1** and **2** in the first and second run (entry 4). Moderate activity (TOF = 35) and exclusive formation of **1** were seen in the

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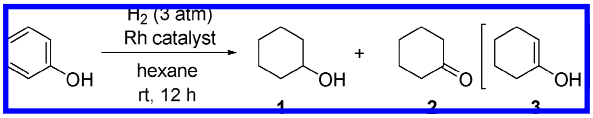
(5) (a) Motoyama, Y.; Takasaki, M.; Higashi, K.; Yoon, S.-H.; Mochida, I.; Nagashima, H. *Chem. Lett.* **2006**, *35*, 876. (b) Takasaki, M.; Motoyama, Y.; Higashi, K.; Yoon, S.-H.; Mochida, I.; Nagashima, H. *Chem. Asian J.* **2007**, *2*, 1524. (c) Takasaki, M.; Motoyama, Y.; Yoon, S.-H.; Mochida, I.; Nagashima, H. *J. Org. Chem.* **2007**, *72*, 10291. (d) Takasaki, M.; Motoyama, Y.; Higashi, K.; Yoon, S.-H.; Mochida, I.; Nagashima, H. *Org. Lett.* **2008**, *10*, 1601.

(6) Representative papers for arene hydrogenation under mild conditions: (a) Yang, H.; Gao, H.; Angelici, R. J. *Organometallics* **2000**, *19*, 622. (b) Maegawa, T.; Akashi, A.; Sajiki, H. *Synlett* **2006**, 1440. (c) Maegawa, T.; Akashi, A.; Yaguchi, K.; Iwasaki, Y.; Shigetsura, M.; Monguchi, Y.; Sajiki, H. *Chem. Eur. J.* **2009**, *15*, 6953.

(7) Park, I. S.; Kwon, M. S.; Kim, N.; Lee, J. S.; Kang, K. Y.; Park, J. *Chem. Commun* **2005**, 5667.

Table 2. Recycle Experiments in Hydrogenation of Phenol with Rh Catalysts[a]



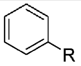
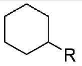
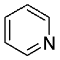
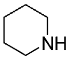
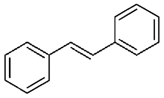
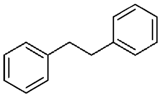
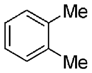
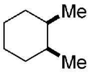
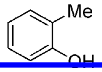
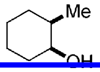
		convn (%); [TOF[b]]; {**1/2**}		
entry	catalyst	1st run	2nd run	3rd run
1	Rh/CNF-P	78 [170] {45:55}	70 [150] {31:69}	
2	Rh/CNF-T	>99 [>860] {>99:<1}	>99 [>860] {>99:<1}	>99 [>860] {>99:<1}
3	Rh/C[c]	>99 [>35] {>99:<1}	17 [5] {12:88}	
4	Rh/C[c]	31 [11] {32:68}	31 [11] {22:78}	
5	Rh/C[c]	<1 [−] {−}	<1 [−] {−}	

[a] All reactions were carried out with phenol (1 mmol) and Rh/CNF catalyst (5 mg) in hexane (1 mL) at room temperature for 12 h under H_2 (3 atm). The yield was determined by GLC analysis. [b] TOF = mol (product)/mol (Rh)•h. [c] Three commercially available Rh/C catalysts purchased from three different sources (5 wt %) were used.

Rh/C shown in entry 3; however, significant retardation of the catalytic activity and a decrease in selectivity of **1** were apparently problematic in the second run. Two Rh/CNFs were subjected to the hydrogenation under the same conditions. As shown in entry 2, Rh/CNF-T afforded the best results among those we examined in the catalyst efficiency and selectivity of **1**, and of particular importance is that the good catalyst performance was reproduced in the second and third runs.[10] Furthermore, ICP-MS analysis of the product obtained in each cycle has shown that the amount of Rh-leaching from CNF-T was below the detection limit (<0.3 ppm).

The utility of Rh/CNF-T is demonstrated by the hydrogenation of substituted aromatic compounds as shown in Table 3. The reaction was carried out in the presence of Rh/CNF-T as a catalyst ($S/C = 10{,}300$) at ambient temperature under H_2 (initial pressure: $P_{H_2} = 3$ atm). It should be noted that the substrates underwent hydrogenation over Ru/CNF-P ($S/C \leq 14{,}000$, 100 °C, $P_{H_2} = 30$ atm) as previously reported;[5b] however, the activity of Ru/CNFs is in most cases lower than that of Rh/CNF-T under the reaction conditions shown in Table 3. The substituents on an aromatic ring affected the reaction rate. The hydrogenation of arenes with electron-donating groups such as toluene, phenol, and anisole smoothly proceeded under the conditions to afford the corresponding cyclohexane derivatives in quantitative yields (entries 1−3). In contrast, the reaction of ethyl benzoate was relatively slower, whereas that of acetophenone was accompanied by formation of 1-phenylethanol and recovery of the starting material. Starting materials were completely recovered in the reaction of benzonitrile and nitrobenzene (entries 4−7). Nitrogen-containing substituent seemed to poison the catalyst;[11] the reaction of pyridine required both higher temperature (70 °C) and hydrogen pressure (10 atm). No leaching of Rh was observed in the product, whereas TEM analysis indicates no sintering of the nanoparticles on the support after the reaction (entry 8). Reaction of a C═C bond was preceded by the arene hydrogenation; *trans*-stilbene was selectively converted to 1,2-diphenylethane (entry 9). Disubstituted *o*-xylene and *o*-cresol were also hydrogenated in good to high yields under these conditions. (entries 10 and 11).

Table 3. Hydrogenation of Various Arenes with Rh/CNF-T[a]

entry	substrate	product	yield (%)[b]
			
1	R = Me		>99
2	R = OH		>99
3	R = OMe		>99
4	R = CO_2Et		85
5	R = COMe		5[c]
6	R = CN		0
7	R = NO_2		0
8[d]			76[e]
9			>99
10			95 (88% *cis*)
11			85 (65% *cis*)

[a] All reactions were carried out with aromatic compound (1 mmol) and Rh/CNF-T (5 mg; 0.2 wt % Rh; $S/C = 10{,}300$) in hexane (1 mL) at rt for 12 h under H_2 (3 atm). [b] Determined by GLC analysis with *n*-decane or *n*-dodecane as an internal standard because these products are volatile. [c] The reaction was accompanied by hydrogenation to a ketone to alcohol to give 1-phenylethanol (13%). [d] At 70 °C under 10 atm of H_2. [e] Determined by ^1H NMR analysis.

A highlight of the catalyst performance of Rh/CNF-T is successful hydrogenation of arenes containing a glycidyl ether moiety, in which aromatic hydrogenation proceeds with the epoxido group remaining intact. Epoxides are important synthetic intermediates in organic synthesis.[12] From an idustrial point of view, epoxides exemplified by easily accessible glycidyl ethers are important components of epoxido resins, and various epoxides are subjected to practical usage as monomers, comonomers, and bridging reagents.[13] Selective hydrogenation of an aromatic ring in

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(8) (a) Pellegatta, J.-L.; Blandy, C.; Collière, V.; Choukroum, R.; Chaudret, B.; Cheng, P.; Philippot, K. *J. Mol. Catal. A: Chem.* **2002**, *178*, 55. (b) Roucoux, A.; Schulz, J.; Patin, H. *Adv. Synth. Catal.* **2003**, *345*, 222.

(9) Similar TOF (250 [mol (benzene)/mol (Rh)•h]) was reported in experiments using polymer-stabilized rhodium nanoparticles (Rh/PVP) at 30 °C under 7 atm of H_2; see ref 8a.

(10) Other recyclable rhodium catalysts: (a) Mu, X.-D.; Meng, J.-Q.; Li, Z.-C.; Kou, Y. *J. Am. Chem. Soc.* **2005**, *127*, 9694. (b) Falini, G.; Gualandi, A.; Savoia, D. *Synthesis* **2009**, 2440.

(11) Reviews: (a) Weissernicl, K.; Arpe, H. J. *Industrial Organic Chemistry*, 2nd ed.; VCH: New York, 1993; p 343. (b) Stanislaus, A.; Cooper, B. H. *Catal. Rev. Sci. Eng.* **1994**, *36*, 75. (c) Augustine, R. L. *Heterogeneous Catalysis for the Synthetic Chemist*; Marcel Dekker: New York, 1996; Chapter 17. (d) Harman, W. D. *Chem. Rev.* **1997**, *97*, 1953. (e) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *191*, 187. (f) Dyson, P. J. *Dalton Trans.* **2003**, 2964.

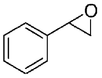
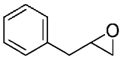
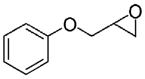
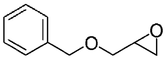
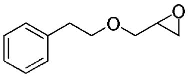
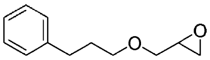
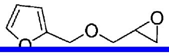
(12) *Aziridines and Epoxide in Organic Synthesiss*; Yudin, A. K., Ed.; Wiley-VCH: Weinheim, 2006.

the vicinity of an epoxido group is a challenge to be developed for preparation of the corresponding cyclohexane derivatives containng the epoxido group. However, the reaction has a problem of epoxide opening, which is easily promoted by acid, base, and H_2 activated by transition metal catalysts.[14] Accordingly, there have been only a few examples of catalytic arene hydrogenation with good to high selectivity. Lemaire and co-workers reported that the hydrogenation of phenyl glycidyl ether by a $RuCl_3$/trioctylamine system ($S/C = 40$) proceeded at room temperature to give cyclohexyl glycidyl ether selectively in 70% yield.[15a] Hara and Inagaki reported that Rh/graphite catalyzed the hydrogenation of phenyl glycidyl ether ($S/C = 1{,}370$) and bisphenol A bisglycidyl ether ($S/C = 600$) at 85 °C to afford the corresponding alicyclic compounds with 91% and 97% selectivity.[15b] In both cases, however, application of high hydrogen pressure (50−70 atm) was necessary. Hydrogenation of benzyl glysidyl ether over Ru/CNF-P, which as we reported shows high activity toward arene hydrogenation,[5a−c] could not solve the problems of either activity or selectivity.

Catalytic hydrogenation of various arenes containing an epoxido group were carried out with Rh/CNF-T ($S/C = 2{,}620$) under H_2 (10 atm), and the results are summarized in Table 4. Although the reaction of styrene oxide (**4a**) afforded a mixture of products containing ethylcyclohexane and phenylethanols due to concomitantly occurring hydrogenolysis of C−O bonds (entry 1), that of allylbenzene oxide (**4b**) gave the corresponding allylcyclohexane oxide (**5b**). The reaction was not fast, and the yield reached 30% after 24 h as shown in entry 2. In sharp contrast, glycidyl ethers **4c**−**g**, smoothly underwent the hydrogenation under these conditions to afford the corresponding alicyclic epoxides (**5c**−**g**) in almost quantitative yields. Besides Rh/CNF-T, the Rh/CNF-P was also useful for hydrogenation of **4d** (entry 5). It is noteworthy that reductive cleavage of a benzylic C−O bond, which potentially occurs in the hydrogenation of **4d** and **4g**, was not observed at all (entries 4 and 9). Furthermore, the reaction of optically active benzyl glycidyl ether **4d** (>99% ee, *R*) involved no racemization, affording (*R*)-cyclohexylmethyl glycidyl ether **5d** (entry 6).

In summary, we have found that Rh/CNFs are easily prepared from $Rh_4(CO)_{12}$ and CNFs. Among them, Rh/CNF-T is a highly active and reusable catalyst for arene hydrogenation, which proceeds under mild conditions in high turnover numbers. The catalytic activity is not decreased in repeated experiments, and there is no leaching of the rhodium species to the product. Utility of the Rh/CNF-T is demonstrated in hydrogenation of arenes containing epoxido group, which proceeds without promoting the epoxido opening. We are now investigating the further use of CNFs as effective supports for various transition-metal nanoparticles.

Table 4. Hydrogenation of Various Arenes **4a**−**g** Containing an Epoxido Group[a]

entry	substrate		product	yield (%)[b]
1	(±)-**4a**		(±)-**5a**	–[c]
2[d]	(±)-**4b**		(±)-**5b**	30[e]
3	(±)-**4c**		(±)-**5c**	98
4	(±)-**4d**		(±)-**5d**	>99
5[f]	(±)-**4d**		(±)-**5d**	76
6	(*R*)-**4d**		(*R*)-**5d**	99 (>99% ee)[g]
7	(±)-**4e**		(±)-**5e**	>99
8	(±)-**4f**		(±)-**5f**	>99
9	(±)-**4g**		(±)-**5g**[h]	99

[a] All reactions were carried out with **4** (0.5 mmol) and Rh/CNF-T (10 mg; [Rh] = 0.2 wt %) in hexane at room temperature under H_2 (10 atm). [b] Isolated yield. [c] Complicated mixtures were obtained. [d] For 24 h. [e] Determined by ^{1}H NMR analysis. [f] Rh/CNF-P was used as a catalyst. [g] Determined by chiral HPLC analysis using Daicel CHIRALPAK AS-H. [h] The product is tetrahydrofurfuryl glycidyl ether (ca. 1:1 diastereo mixtures).

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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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