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Ruthenium Nanoparticles on Nano-Level-Controlled Carbon Supports as Highly Effective Catalysts for Arene Hydrogenation

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Abstract: The reaction of three types of carbon nanofibers (CNFs; platelet: CNF-P, tubular: CNF-T, herringbone: CNF-H) with [$Ru_3(CO)_{12}$] in toluene heated at reflux provided the corresponding CNF-supported ruthenium nanoparticles, Ru/CNFs (Ru content = 1.1–3.8 wt %). TEM studies of these Ru/CNFs revealed that size-controlled Ru nanoparticles (2–4 nm) exist on the CNFs, and that their location was dependent on the surface nanostructures of the CNFs: on the edge of the graphite layers (CNF-P), in the tubes and on the surface (CNF-T), and between the layers and on the edge (CNF-H). Among these Ru/CNFs, Ru/CNF-P showed excellent catalytic activity towards hydrogenation of toluene with high reproducibility; the reaction proceeded without leaching of the Ru species, and the catalyst was reusable. The total turnover number of the five recycling experiments for toluene hydrogenation reached over 180 000 (mol toluene) (mol Ru)$^{-1}$. Ru/CNF-P was also effective for the hydrogenation of functionalized benzene derivatives and pyridine. Hydrogenolysis of benzylic C–O and C–N bonds has not yet been observed. Use of poly(ethylene glycol)s (PEGs) as a solvent made possible the biphasic catalytic hydrogenation of toluene. After the reaction, the methylcyclohexane formed was separated by decantation without contamination of the ruthenium species and PEG. The insoluble PEG phase containing all of the Ru/CNF was recoverable and reusable as the catalyst without loss of activity.

Keywords: arenes · carbon · hydrogenation · nanostructures · ruthenium

Introduction

Arene hydrogenation is an important method of organic transformation on both laboratory and industrial scales; it realizes the facile production of substituted cyclohexane derivatives and the removal of aromatic compounds from fuels.[1] In general, the reactions are performed by using heterogeneous catalysts that consist of transition-metal particles dispersed on solid supports with a large surface area. It is known that rhodium compounds are generally more active than other catalysts on solid supports. Although the catalytic activity for arene hydrogenation decreases in the order Rh > Ru > Pt > Ni > Pd > Co,[1c] inexpensive Ru, Ni, or Pd catalysts are commonly used at high reaction temperatures under high H_2 pressures in industrial processes owing to their high thermal stability. These heterogeneous catalysts are easily separated from the product, and the recovered catalysts are recyclable. However, insufficient selectivity and metal leaching are problems yet to be solved.

The use of homogeneous catalysts, for which catalytic activity and selectivity of the reaction are tunable by the choice of appropriate ligands, may be a good alternative. However, these catalysts generally show poor activity for arene hydrogenation.[2] Recently, several homogeneous catalysts in the literature that showed good activity were reinvestigated, and it was concluded that soluble nanometal particles are involved as the active catalyst species.[3,4] In a typical example, Rh nanoparticles with high dispersity and narrow size distributions stabilized by appropriate surfactants showed higher activity and selectivity for the hydrogenation of monocyclic arenes than conventional heterogene-

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ous catalysts.[1e,3a] In other words, the application of size-controlled nanoparticles to catalysts on solid supports may improve the activity problem of heterogeneous catalysts;[5,6] such heterogeneous nanocatalysts are expected to solve the inherent problems of soluble metal-nanoparticle catalysts such as poor thermal stability, problematic separation of the catalyst, and precipitation of the catalyst when the polarity of the solution changes.

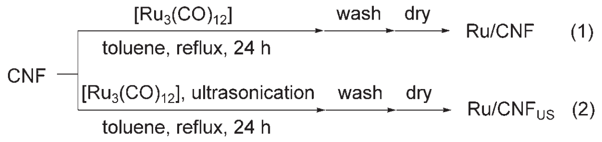
In this context, we are interested in heterogeneous catalysts in which size-controlled metal nanoparticles are highly dispersed on carbon materials with fine surface structures. It is known that the catalytic properties of metal nanoparticles are dependent on the surface structure of the solid supports. Carbon materials are important solid supports; in particular, the immobilization of transition-metal particles on activated carbon (AC) of large surface area (800–1200 $m^2 g^{-1}$) rather than on silica or alumina leads to the production of more-stable heterogeneous catalysts in both acidic and basic media.[7a] A disadvantage of AC is the existence of a wide variety of surface and pore structures; the ill-controlled surface structures often cause a lack of reproducibility of catalyst performance.[7] In this sense, carbon nanofibers (CNFs) are potentially attractive solid supports for heterogeneous catalysts as they have nano-level-controlled surface structures with moderate surface areas (25–300 $m^2 g^{-1}$).[8] Selective syntheses of three types of CNFs, in which the graphite layers are perpendicular (platelet: CNF-P), parallel (tubular: CNF-T), and stacked obliquely (herringbone: CNF-H), were recently discovered on a large scale by our group.[9] Of particular interest is the high content of reactive "nanosized edge" sites of CNF-P and CNF-H, which is expected to interact with the nanosized metal and contribute to the stabilization of the nanoparticles on the surface.[10] A remaining problem is how to immobilize transition-metal nanoparticles of uniform size on the surface of CNFs with high dispersion. Conventional heterogeneous catalysts are generally prepared by the incipient wetness method to immobilize metal salts on the supports followed by reduction of the salts with hydrogen at high temperature; however, the process sometimes causes aggregation of the metallic species, thus giving rise to a broad particle-size distribution.[11] Size-controlled metal nanoparticles can also be synthesized by the chemical reduction of metal salts by metal hydride reagents such as $NaBH_4$ in the presence of organic surfactants.[12] Immobilization of the surfactant-stabilized nanoparticles on the solid supports causes contamination of residual reductants and surfactants on the supports.

We recently found that highly dispersed and size-controlled ruthenium nanoparticles supported on CNFs (Ru/CNF catalysts) can be synthesized by pyrolysis of a zero-valent organometallic complex, $[Ru_3(CO)_{12}]$. These Ru/CNFs showed good catalytic activity for arene hydrogenation, and Ru/CNF-P showed the highest catalytic activity and efficiency without leaching of the Ru species. Our preliminary account appeared earlier;[13] we describe herein the full details of the synthesis of the Ru/CNF catalysts from $[Ru_3(CO)_{12}]$ and their catalytic performance in arene hydrogenation, including reactivity, reproducibility, and durability. Furthermore, we report a new finding that the use of poly(ethylene glycol) (PEG) as a solvent leads to an effective biphasic reaction system, which takes part in facile recovery and reuse of the catalyst. On the basis of these results, the effects of nano-level-controlled carbon supports for heterogeneous catalysts are discussed.

Results and Discussion

Synthesis and Characterization of Ru/CNFs

It is known that $[Ru_3(CO)_{12}]$ readily eliminates its CO ligands to form larger cluster molecules under mild conditions.[14] In particular, the reaction of $[Ru_3(CO)_{12}]$ in the presence of arenes affords hexaruthenium carbonyl clusters that bear the arene as a ligand. It is also known that pyrolysis of $[Ru_3(CO)_{12}]$ in certain solvents is an attractive synthetic method for metal particles.[15] As partial structures of CNFs are giant aromatic compounds, we are interested in the possibility that pyrolysis of $[Ru_3(CO)_{12}]$ in the presence of CNFs in solution may be a good means of immobilizing ruthenium nanoparticles on the surface of CNFs. The CNF-supported Ru catalysts were actually prepared by the following methods (Scheme 1). Thermal decomposition of $[Ru_3(CO)_{12}]$ (31.9 mg, [Ru] = 15.1 wt% for the support) in the presence of three types of carbon nanofibers in toluene heated at reflux followed by filtration and washing with toluene and diethyl ether afforded the corresponding Ru/CNF-P, Ru/CNF-H, and Ru/CNF-T, respectively (Scheme 1, (1)). Immobilization of the Ru species on the commercially available activated carbon (Ru/AC) was performed by the same technique. As an alternative, sonication, which was recently reported by Bunker and Karnes as a good method for the preparation of nanoparticles from $[Fe(CO)_5]$,[16] was exam-



Scheme 1. Preparative method for the Ru/CNF catalysts.

Abstract in Japanese:

ナノレベルで表面構造が制御された3種類の炭素ナノ繊維(CNF)存在下、$[Ru_3(CO)_{12}]$をトルエン中加熱することで、(CNF)上に粒子径2–4nmのルテニウム微粒子を担持することに成功した。中でもplatelet型CNFに担持したRu/CNF-Pは、1.6–1.7wt%のルテニウム微粒子がグラファイト層のエッジ部に選択的かつ均質に担持されていた。このRu/CNF-Pは芳香族化合物の環水素化反応において高い触媒活性、ならびに繰り返し耐久性を示すと共に、副反応を伴うことなく、さらに生成物中への金属の溶出は観測されなかった。さらにPEGを溶媒に用いた2相系反応とすることで、簡便な生成物の分離と触媒の再利用が可能となった。

ined for the preparation of Ru/CNF-P; treatment of [$Ru_3(CO)_{12}$] with CNF-P by ultrasonic disruptor (active time with 0.5 s on, 0.5 s off) in toluene heated at reflux gave the desired product (Ru/CNF-P_{US}) (Scheme 1, (2)).

The Ru content of the Ru/CNFs and Ru/AC was determined to be 1.0–3.8 wt % by inductively coupled plasma (ICP) MS analysis (Table 1). Up to 25 % of charged ruthenium was immobilized on the surface of the CNFs or AC by this method, and the remaining ruthenium species, which included a large ruthenium cluster, was recovered from the filtrate.[17] The Ru content was constant in several samples of Ru/CNF-P (1.6–1.7 wt %) and Ru/AC (1.3–1.4 wt %) (Table 1, entries 1 and 4). In contrast, those of Ru/CNF-H and Ru/CNF-T were not very reproducible (1.1–3.8 wt % for Ru/CNF-T, 1.1–1.6 wt % for Ru/CNF-H; Table 1, entries 2 and 3). Ru/CNF-P_{US} contained 1 wt % of Ru (Table 1, entry 5).

Table 1. Amount of Ru on CNFs and AC.

Entry	Catalyst	Ru [wt %] Calcd	Ru [wt %] Found[a]
1	Ru/CNF-P	15.1	1.6–1.7
2	Ru/CNF-H	15.1	1.1–1.6
3	Ru/CNF-T	15.1	1.1–3.8
4	Ru/AC	15.1	1.3–1.4
5	Ru/CNF-P_{US}	15.1	1.0

[a] Determined by ICP-MS analysis.

The transmission electron microscopy (TEM) images of these Ru/CNFs and Ru/AC showed that the ruthenium nanoparticles are dispersed with narrow size distributions, but their locations are highly dependent on the surface structure of the supports. On CNF-P, small and spheroidal species ($d = (2.5 \pm 1)$ nm) are homogeneously dispersed selectively on the edge of the graphite layers (Figure 1, A).[10] In sharp contrast, the TEM images of the other Ru/CNFs showed that the majority of particles are in the size range of 2–4 nm; however, some large Ru masses ($10 < d < 50$ nm for Ru/CNF-T, $50 < d < 150$ nm for Ru/CNF-H) were observed to coexist. The nanoparticles of Ru/CNF-T are located both in the tubes and on the surface (Figure 1, C), whereas they exist between the graphite layers and on the edge in Ru/CNF-H (Figure 1, B). In Ru/AC, the nanoparticles are dispersed, and most of the Ru particles are located not on the surface but inside the pores (Figure 1, D). As described above, sonication is not effective for increasing ruthenium content, but is an excellent method for controlling particle size; the TEM image of Ru/CNF-P_{US} revealed that particles of average size 2.1 nm were formed with a rather narrow size distribution ($d = 1.5$–2.6 nm) (Figure 2, E).

X-ray photoelectron spectroscopy (XPS) analysis showed that there is a high content of the Ru^0 species on the surface of the freshly prepared Ru/CNFs ($Ru^0/Ru^{IV} = 74{:}26$–$41{:}59$; Table 2 and Figure 3). The Ru^0/Ru^{IV} ratio decreased in the order CNF-P > CNF-T > CNF-H > AC; this order is similar to the degree of graphitization.[9] The ruthenium species was slowly oxidized under aerobic conditions; the Ru^0/Ru^{IV} ratio changed to 57:43–2:98 after six months. Notably, the Ru^0 species on CNF-T, CNF-H, and AC was oxidized relatively quickly, but Ru/CNF-P and Ru/CNF-P_{US} were resistant to oxidation.

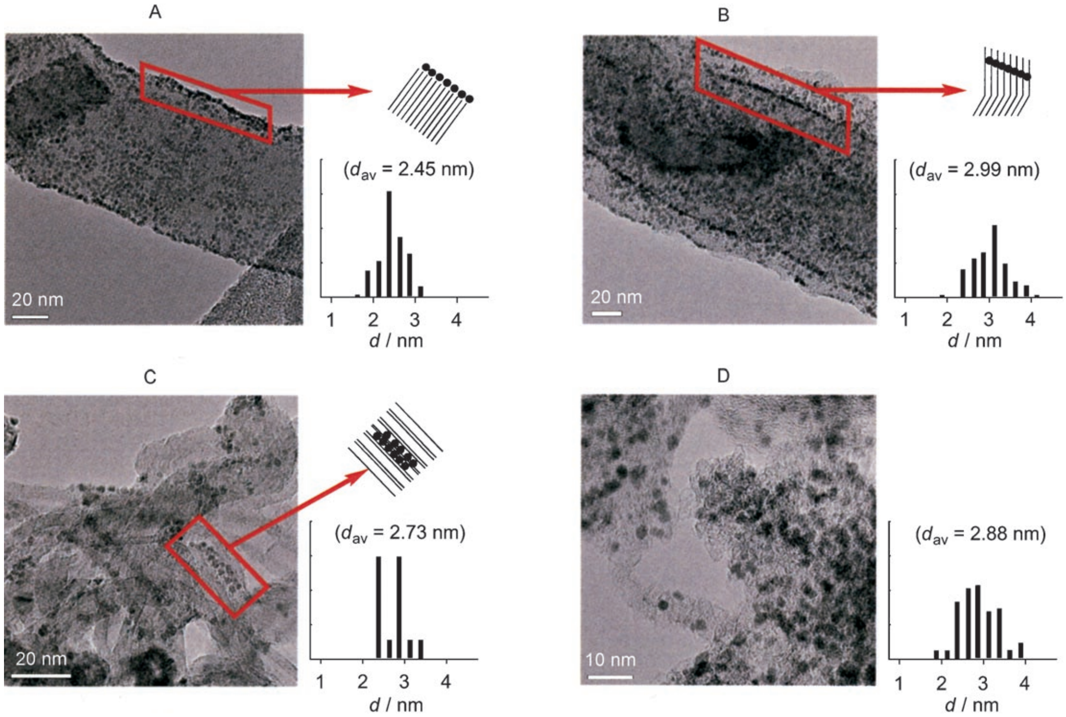


Figure 1. TEM images and histograms of the Ru particles. A) Ru/CNF-P, B) Ru/CNF-H, C) Ru/CNF-T, D) Ru/AC.

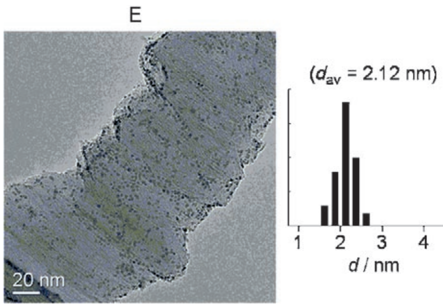


Figure 2. TEM image and histogram of the Ru particles of Ru/CNF-P_{US}.

Table 2. Ru^0/Ru^{IV} area ratios of Ru/CNFs and Ru/AC by XPS.

Entry	Catalyst	XPS area ratio (Ru^0/Ru^{IV}) As prepared	After 6 months
1	Ru/CNF-P	74:26	57:43
2	Ru/CNF-H	57:43	21:79
3	Ru/CNF-T	69:31	2:98
4	Ru/AC	41:59	15:85
5	Ru/CNF-P_{US}	62:38	41:59

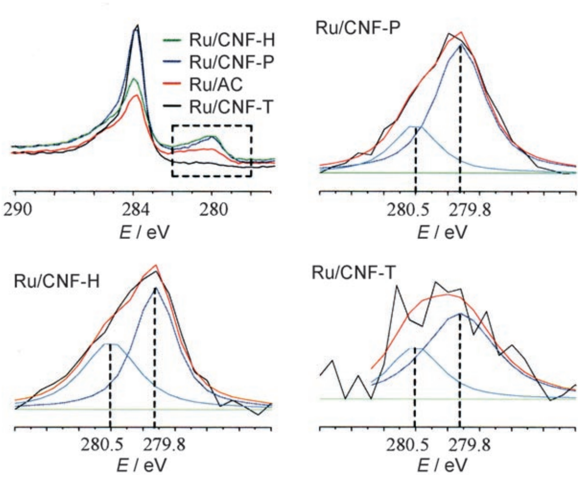


Figure 3. XPS survey scans of Ru nanoparticles.

Thus, the present organometallic approach provided an important discovery that CNF-P, in which the graphite layers are stacked perpendicularly, is the most effective type of carbon nanofibers for anchoring monodispersed ruthenium nanoparticles on the surface with a narrow size distribution. Simple heating or sonication in toluene is a reproducible preparative method for CNF-P-immobilized ruthenium nanoparticles. Of particular interest is the higher content of the Ru^0 species in Ru/CNF-P and Ru/CNF-P_{US}, which were not quickly oxidized. It is known that the active species for catalytic hydrogenation are low-valent, highly dispersed smaller spherical metal particles, which have a large catalytically active surface area. Thus, Ru/CNF-P and Ru/CNF-P_{US} are apparently good candidates for a new and efficient catalyst for arene hydrogenation.

Hydrogenation of Aromatic Compounds

The catalytic activities of the CNF-supported Ru catalysts synthesized were examined by toluene hydrogenation as a standard reaction. Hydrogenation of toluene was typically performed in a 100-mL stainless autoclave under H_2 (initial pressure: $P_{H2} = 30$ atm) (Table 3). A notable feature of the Ru/CNF catalysts is that Ru/CNF-P has a particularly higher catalytic activity at lower temperatures than the conventional heterogeneous ruthenium catalysts, with which arene hydrogenation is usually performed at over 150 °C.[18] At 100 °C, both Ru/CNF-P and Ru/CNF-P_{US} smoothly catalyzed the reduction of toluene to afford methylcyclohexane as a single product in quantitative yield. No induction period was observed, and the turnover frequencies (TOFs) of these catalysts were greater than 12 000 (mol toluene) $(mol\ Ru)^{-1}\ h^{-1}$. In particular, the turnover number (TON) of the Ru/CNF-P_{US}-catalyzed reaction reached 61 000 (mol toluene) $(mol\ Ru)^{-1}$ (Table 3, entries 1 and 5). Excellent catalytic activity was also observed for the CNF-P-supported Ru catalyst in the reaction at lower temperature; the TOF of the Ru/CNF-P catalyst was over 10^4 (mol toluene) $(mol\ Ru)^{-1}\ h^{-1}$ even at 40 °C (Table 3, entry 7). In our long search, the most active arene-hydrogenation catalyst we found in the literature was that of Angelici and co-workers: a Rh–bipyridyl complex tethered to a Pd/SiO_2 catalyst.[19] This catalyst is active by the synergistic action of both the Rh complex and the Pd particles on the support, and the TON and TOF of the toluene hydrogenation at 70 °C were 14 500 (mol toluene) $(mol\ Rh)^{-1}$ and 2870 (mol toluene) $(mol\ Rh)^{-1}\ h^{-1}$, respectively. The Ru/CNF-P and Ru/CNF-P_{US} catalysts are apparently more active than the Angelici catalyst. Another feature of the Ru/CNF-P catalysts is reproducibility over 10 experiments; there is little difference in TOF among the experiments. In sharp contrast, the hydrogenation over Ru/CNF-T, Ru/CNF-H, or Ru/AC sometimes showed comparable catalytic activity to that with Ru/CNF-P at 100 °C, but there was poor re-

Table 3. Hydrogenation of toluene catalyzed by Ru catalysts.[a]

Entry	Catalyst	T [°C]	t [h]	Conv.[b] [%]	TOF[c]
1	Ru/CNF-P	100	2.5	>99	≈14 200
2	Ru/CNF-H	100	5	0–99[d]	–
3	Ru/CNF-T	100	5	3–99[d]	–
4	Ru/AC	100	5	0–90[d]	–
5	Ru/CNF-P_{US}	100	5	>99	≈12 200
6	Ru/C[e]	100	5	24–99	600–2400
7[f]	Ru/CNF-P	40	1	89–94	≈11 000
8[f]	Ru/CNF-H	40	1	9–24	–
9[f]	Ru/CNF-T	40	1	<1	–
10[f]	Ru/C[e]	40	1	<1	–

[a] All reactions were carried out with toluene (3 mL) and ruthenium catalyst (5 mg) under H_2 (30 atm). [b] Determined by capillary GLC analysis. [c] TOF in (mol toluene) $(mol\ Ru)^{-1}\ h^{-1}$. [d] A small amount of methylcyclohexene was formed. [e] Purchased from N. E. CHEMCAT Co. (5 wt % Ru). [f] Toluene (1 mL) was used.

producibility (Table 3, entries 2–4). At 40 °C, the catalytic activity of Ru/CNF-H was much lower than that of Ru/CNF-P, whereas both Ru/CNF-T and commercially available Ru/C catalysts were inactive to hydrogenation under the same conditions (Table 3, entries 8–10).[18] These results clearly demonstrate the excellent activity and durability of Ru/CNF-P.

The Ru/CNF-P catalyst is reusable. After the toluene hydrogenation (substrate/catalyst molar ratio, S/C = 35 800) was performed at 100 °C for 5 h, the catalyst was recovered by filtration and subjected to a further run of hydrogenation. Even after the fifth run, toluene was completely converted into methylcyclohexane; the sum of the TONs for the five repeated toluene hydrogenations by the Ru/CNF-P catalyst was over 180 000. A clue for understanding this high reusability of Ru/CNF-P is available from the TEM images of Ru-CNF-P, which was recovered from the reaction mixture. The TEM image of the Ru/CNF-P catalyst used for five cycles of reaction at 40 °C showed some aggregation of Ru species, but the average diameter of Ru particles was still below 3 nm (Figure 4, left). In contrast, aggregation of particles was observed for both Ru/CNF-H and Ru/CNF-T, which were recovered from the reactions of three repeated runs at 40 °C (Figure 4, center and right). In the three cycles of the reuse experiments, Ru/CNF-H decreased in catalytic activity, whereas Ru/CNF-T showed little activity even for the first run. These results suggest that CNF-P is an excellent support for ruthenium nanoparticles for preventing aggregation, which causes a decrease in catalytic activity.

An interesting observation was made by measuring the hydrogen uptake of Ru/CNF-P-catalyzed hydrogenation of toluene at 100 °C under 10 atm of initial hydrogen pressure. Under these conditions, an induction period ($\approx$100 min) was observed, but toluene was completely consumed within 6 h to give the product in quantitative yield (TON = 11 200). The induction period was shorter in the recycling experiments; in a typical example, the Ru/CNF-P catalyst used for five cycles of reaction showed an induction period of about 20 min, and the reaction was completed within 4 h. The induction period was apparently dependent on the content of low-valent ruthenium species on the surface; the Ru/CNF-P catalyst recovered after the fifth run contained 85 % of the Ru^0 species (XPS analysis), which was higher than that of the virgin catalyst (74 %). These results suggest that CNF-P is a good support for the Ru^0 species active for the hydrogenation. As an application, the Ru^0 species was generated by preactivation of Ru/CNF-P by hydrogen (30 atm, 40 °C, 1 h). The formed “preactivated Ru/CNF-P” showed higher catalytic activity than the original catalyst, which enables the reaction to be performed even at ambient temperature under hydrogen atmosphere (1 atm); the TOF of the reaction under these conditions was about 60 (mol toluene) $(\text{mol Ru})^{-1}\,h^{-1}$.

The excellent property of CNF-P as the catalyst support offers a solution to problematic metal leaching in heterogeneous hydrogenation; this is particularly important in process chemistry for the production of medicines, in which contamination of the product by metals is severely restricted because of their influence on the human body.[20] There was no detectable Ru species in the product obtained by each recycling experiment of the Ru/CNF-P-catalyzed hydrogenation of toluene (ICP-MS experiments). These results clearly show that CNF-P tightly anchors the catalytically active Ru nanoparticles onto the surface.

The Ru/CNF-P catalyst is also effective towards hydrogenation of various aromatic compounds. It is well-known that the reactivity of the arenes that bear electron-withdrawing groups is lower than that of benzene or toluene. It is also known that coordination of nitrogen in aminoarenes and nitrogen heterocycles to the metal center poisons the catalytic activity.[1,21] For instance, TOFs of the reaction with the Angelici catalyst decreased in the order toluene (2880) > ethyl benzoate (1510) > ethyl 4-methylbenzoate (500).[18] A serious side reaction in the hydrogenation of phenyl ethers, aniline, and benzylalcohol and amines is hydrogenolysis leading to the cleaving of C−O or C−N bonds in the molecule, which causes the formation of some by-products.[22,23] The Ru/CNF-P catalyst generally showed high catalytic efficiency for the hydrogenation of functionalized benzene derivatives and pyridine (Table 4). The TOFs are comparable to the Angelici Pd/SiO_2-immobilized Rh complex[18] and are higher in some cases. For example, TOFs were 1660 and 1490 in the Ru/CNF-P-catalyzed hydrogenation of ethyl benzoate and ethyl 4-methylbenzoate, respectively (Table 4, entries 2 and 3). In all the reactions in Table 4, no side reaction was observed. Typically, anisole and diphenylether were com-

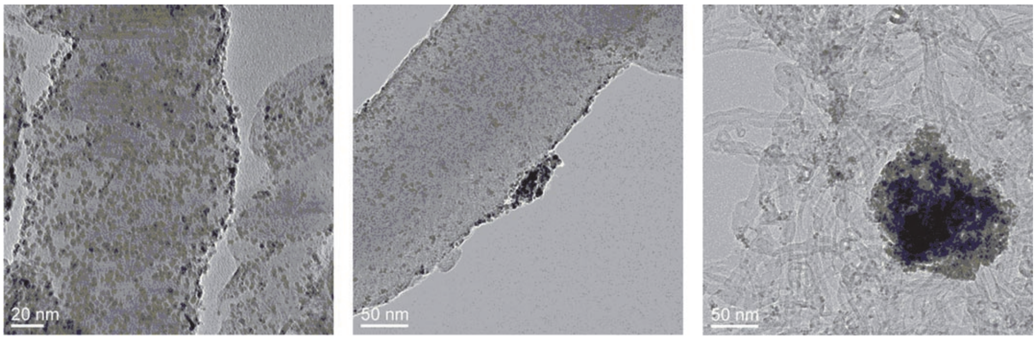
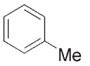
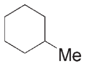
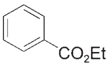
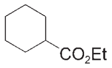
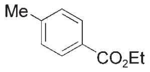
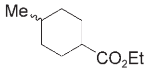
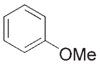
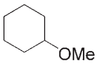
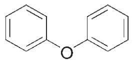
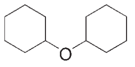
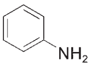
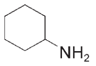
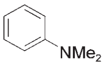
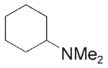
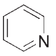
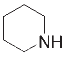
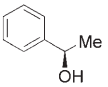
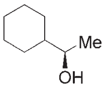
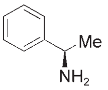
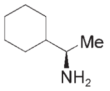


Figure 4. TEM images of the recovered Ru/CNF-P (left), Ru/CNF-H (center), and Ru/CNF-T (right).

Table 4. Reduction of various aromatic compounds by Ru/CNF-P.[a]

Entry	Substrate	*t* [h]	Product	Yield[b] [%]	TON[c]
1[d]		2.5		> 99	35 800
2		5		> 99	8300
3		5		> 99	7460
4		5		> 99	11 600
5		5		> 99[e]	7970
6		24		> 99[e]	13 900
7		24		> 99[e]	9420
8		24		> 99	13 400
9[f]		3		> 99[g]	5250
10[h]		24		> 99[e,g]	9320

[a] All reactions were carried out with substrate (1 mL) and Ru/CNF-P (1.7 wt % Ru, 5 mg) at 100 °C under H_2 (30 atm). [b] Determined by capillary GLC analysis because many of the products are volatile. [c] TON in (mol substrate)(mol Ru)$^{-1}$. [d] Toluene (3 mL) was used. [e] Determined by ^{1}H NMR spectroscopic analysis. [f] Substrate (0.5 mL) was used under H_2 (20 atm). [g] Optical purity was determined by capillary GLC analysis after conversion into the corresponding acetate (Table 4, entry 9) and acetamide (Table 4, entry 10). [h] THF (2 mL) was used as a solvent.

pletely converted into the corresponding cyclohexyl ethers within 5 h (TOF = 2300 and 1590); hydrogenolysis products such as cyclohexanol and cyclohexane, which often form in the hydrogenation with conventional heterogeneous catalysts, were not detected (Table 4, entries 4 and 5).[21] The reactivity of the nitrogen-containing aromatic compounds, anilines and pyridine, was somewhat lower than that of the others, and a longer reaction time (24 h) was necessary to obtain the product in satisfactory yields (TOF = 390–600; Table 4, entries 6–8). Reduction of aniline is sometimes problematic because of the formation of dicyclohexylamine as a by-product;[22] however, the Ru/CNF catalyst gave cyclohexylamine in quantitative yield without contamination with any by-product (Table 4, entry 6). As hydrogenation is sometimes accompanied by a carbon–carbon double-bond migration or dehydrogenation followed by rehydrogenation, racemization may occur concomitantly in the hydrogenation of optically active molecules. However, no racemization was observed in the hydrogenation of optically pure benzylalcohol and amine by the Ru/CNF-P catalyst: (*R*)-1-phenylethanol and (*R*)-1-phenylethylamine were reduced to the corresponding (*R*)-1-cyclohexylethanol and (*R*)-1-cyclohexylethylamine in quantitative yields without loss of optical purity (> 99 % *ee* in both cases). Furthermore, hydrogenolysis of the benzylic C–O and C–N bonds was not observed in either of the reactions (Table 4, entries 10 and 11).

Catalyst Recycling System

As described above, Ru/CNF-P not only acts as a powerful and robust catalyst for the hydrogenation of various aromatic compounds, it is also useful as a reusable catalyst. As briefly noted above, the catalyst can be recovered by filtration and subjected to a second run; however, we encountered two problems in this recycling process during the repeated recycling experiments. One was the efficiency of filtration. Ru/CNFs are light and fine powdery materials, and it is difficult to recover all of the catalyst used. The other was oxidation of the Ru species during the recycling process when the filtration was carried out under aerobic conditions, which causes the induction period as described above. In this context, it is desirable that the catalyst be recycled by a process other than filtration, and that the recycling runs can be performed under a hydrogen or inert-gas atmosphere. During our studies on arene hydrogenation in various solvent systems, we were aware that the Ru/CNF-P catalyst can be highly dispersed in polar organic compounds and solvents such as ethyl benzoate, aniline, acetonitrile, dimethylformamide, and ethylene glycol; this feature may be useful for application to liquid/liquid biphasic reactions. Elaboration to discover the most appropriate solvent for immobilizing Ru/CNF-P to the liquid support provided us the nice discovery that PEGs are the most effective solvent for biphasic catalytic hydrogenation of arenes with Ru/CNF-P. Two PEGs of different molecular weight, PEG-200 (liquid at room temperature, solid at −78 °C) and PEG-1000 (m.p.: 40–41 °C), were examined as a solvent in standard hydrogenation experiments. In a representative experiment, PEG-1000 (100 mg) was dissolved in toluene (1 mL) at room temperature. Addition of Ru/CNF-P (10 mg) produced a homogeneous dispersion (Figure 5, F), which was subjected to hydrogenation (30 atm) at 100 °C. After 5 h, the conversion of toluene reached over 90 %. Upon cooling to room tempera-

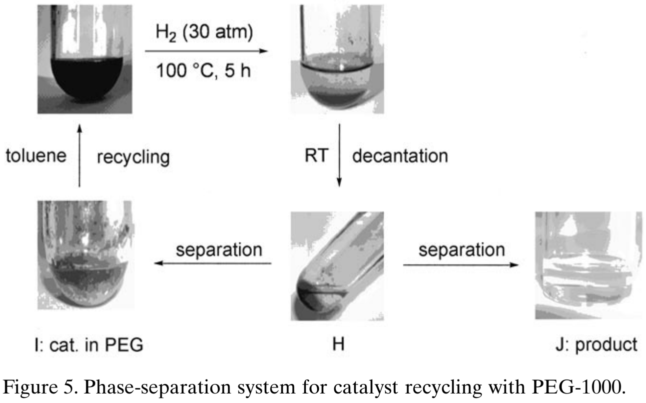


Figure 5. Phase-separation system for catalyst recycling with PEG-1000.

ture, the reaction mixture became biphasic; the upper phase was methylcyclohexane, whereas the lower was resinous PEG-1000 containing the ruthenium catalyst (G). All the charged Ru/CNF-P was completely immobilized in the lower PEG phase, and methylcyclohexane in the upper phase was not contaminated by either PEG or the Ru/CNF-P catalyst. Thus, the desired methylcyclohexane was readily separated from the catalyst in PEG by simple decantation (H and J). The PEG phase containing the separated Ru/CNF-P can be used for further runs (I). This biphasic system proved to be useful for five successive catalyst-recycling experiments without deactivation of the catalyst. The total TON for the five experiments reached over 58700 (mol toluene) (mol Ru)$^{-1}$ (Table 5). We also checked the leaching of the metal species, and ICP-MS analysis showed that no ruthenium was detected in the product. Similarly, the liquid PEG-200 can be used for the biphasic reaction; a mixture of toluene (1 mL) and PEG-200 (1 mL) in the presence of the catalyst (5 mg) was subjected to hydrogenation (30 atm) at 100 °C for 5 h to form the liquid/liquid biphase. After removal of the upper product phase, fresh toluene was added to the residual PEG/catalyst phase, and the mixture was subjected to the next hydrogenation. This protocol was continued for five runs, which resulted in quantitative yields in all experiments. As a similar catalyst-recycling system, Chandrasekhar et al. recently reported the immobilization of Pd/C in liquid PEG-400;[24] this catalyst system was effective for hydrogenation of alkenes and alkynes, as well as debenzylation of benzyl ethers by hydrogenolysis. The catalyst was separated from the product by solidifying the PEG when the reaction mixture was cooled to −78 °C; the product was extracted with diethyl ether.[24a] Our Ru/CNF-P in solid PEG-1000 is advantageous for catalyst separation from the product, which can be achieved at room temperature.

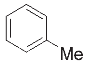
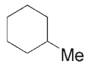
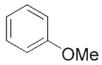
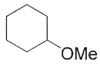
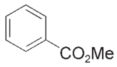
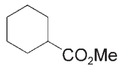
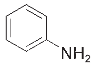
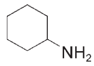
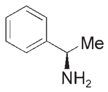
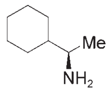
Table 5. Yield (%) of hydrogenation of toluene with Ru/CNF-P in PEG-1000 and PEG-200.[a]

Run	PEG-1000[b] (100 mg)	PEG-200[c] (1 mL)
1	92	>99
2	>99	>99
3	>99	>99
4	>99	>99
5	>99	>99

[a] All reactions were carried out with toluene (1 mL) at 100 °C for 5 h under H_2 (30 atm). [b] 10 mg of catalyst was used. [c] 5 mg of catalyst was used.

This biphasic reaction system with PEGs is also adaptable to the hydrogenation of functionalized benzene derivatives and pyridine. In these hydrogenation reactions, the product is polar and miscible with PEGs. Separation of the product from catalyst/PEG is accomplished by addition of hydrocarbons such as pentane or hexane, which results in phase separation at room temperature. Thus, the first separation of the product is followed by extraction of the PEG phase with the hydrocarbon to give the desired product in satisfactory yields (Table 6, entries 4–8). In the two cases shown in Table 6, entries 7 and 8, the reactions of nitrogen-containing substrates with solid PEG-1000 were sluggish. This was improved by using liquid PEGs, typically PEG-200 or 300; pyridine and (*R*)-1-phenylethylamine were completely reduced for 24 h to afford the corresponding products in pure form (Table 6, entries 7 and 8).

Table 6. Hydrogenation with Ru/CNF-P in PEGs.[a]

Entry	Substrate	PEG	*t* [h]	Product	Conv.[b] [%]	Yield[b] [%]
1		PEG-200	5		>99	>99
2		PEG-300	5		>99	>99
3		PEG-1000	5		>99	>99
4		PEG-300	5		>99	83[c]
5		PEG-300	24		>99	93[c]
6		PEG-1000	24		99	99[c]
7		PEG-300	24		>95[d]	75[c,d]
8		PEG-200	24		>95[d]	70[c,d,e]

[a] All reactions were carried out with substrate (1 mL), Ru/CNF-P (5 mg), and PEG (PEG-200, PEG-300 = 1 mL, PEG-1000 = 100 mg) at 100 °C under H_2 (30 atm). [b] Determined by GLC analysis because many of the products are volatile. [c] After extraction with pentane or hexane. [d] Determined by ^{1}H NMR spectroscopic analysis. [e] Optical purity was determined by capillary GLC analysis after conversion into the acetamide.

Conclusions

We have found that pyrolysis or sonication of $[Ru_3(CO)_{12}]$ in the presence of CNFs is an excellent method for immobilizing the ruthenium nanoparticles on their surface. In particular, the well-controlled surface nanostructure of CNF-P is essential for anchoring the monodispersed Ru nanoparticles with a narrow size distribution. The Ru/CNF-P formed is a highly active and reusable catalyst for arene hydrogenation. The catalytic activity was not decreased in repeated experiments, and there was no leaching of the ruthenium species to the product. The biphasic reaction system, which facilitates catalyst recycling, was established by using PEG as a solvent. These excellent features of Ru/CNF-P were first accomplished by taking advantage of the fine surface structure of CNF-P as the catalyst support. Since the discovery of fullerenes and carbon nanotubes, the science and technology of nanocarbon materials have developed explosively; however, the attempted use of fullerenes and carbon nanotubes (CNTs) as a catalyst support has not yet been successful.

For instance, the C_{60}-supported ruthenium catalyst reported by Schölgl and co-workers has the problem of a small fullerene surface area (5 m^2g^{-1}),[25] and CNTs are generally poor supports for metal anchoring; Planeix et al. reported a CNT (27 m^2g^{-1})-supported Ru catalyst that contained only 0.2 wt% of Ru.[26] The present report clearly demonstrates the utility of the "nano-on-nano approach", that is, immobilization of nanometal particles on a nano-level-controlled carbon support is an excellent method for preparing active and durable heterogeneous catalysts. CNF-P is a particularly good carbon support for metal anchoring, whereas organometallic compounds are good precursors for generating nanometal particles, which are immobilized on the surface of CNF-P. We are now investigating the further use of CNFs as effective catalyst supports for various transition-metal nanoparticles, which includes the exploration of new methods of generation of nanoparticles from organometallic precursors and the application of the synthesized metal/CNFs to the catalytic transformation of organic molecules.

Experimental Section

General

All reactions were carried out under nitrogen or argon atmosphere. All reagents were used as purchased from commercial suppliers without further purification. Solvents were dried and purified by conventional methods prior to use. ^{1}H NMR spectra were recorded on JEOL GSX-270 (270 MHz) and Lambda 400 (395 MHz) spectrometers. ICP-MS analysis was performed at the Center of Advanced Instrumental Analysis, Kyushu University. Gas chromatography (GC) analysis was performed on a Shimadzu GC-17A gas chromatograph equipped with TC-17 (30 m), TC-WAX (30 m), SUPELCO β-DEX 120 (30 m), and β-DEX 325 (30 m) columns. CNF-P, CNF-T, and CNF-H were prepared by the method reported previously.[9] $[Ru_3(CO)_{12}]$ was prepared by the literature method.[27]

Synthesis of the Ru Catalysts

Pyrolysis of $[Ru_3(CO)_{12}]$: $[Ru_3(CO)_{12}]$ (31.9 mg, [Ru] = 15.1 mg) was added to a suspension of CNF or AC (100 mg) in toluene (17 mL) under argon atmosphere. After the mixture was heated under reflux for 24 h, the insoluble carbon materials were isolated by filtration with membrane filters (Durapore HV, 0.45 μm). The solid was washed with toluene (50 mL) and diethyl ether (50 mL) and then dried under vacuum (0.04 Torr) at room temperature for 2 h to afford the corresponding Ru/CNF catalysts.

Ultrasonic disruptor: $[Ru_3(CO)_{12}]$ (31.9 mg, [Ru] = 15.1 mg) was added to a suspension of CNF-P (100 mg) in toluene (17 mL) under argon atmosphere. The mixture was heated under reflux with sonication by a TOMY Ultrasonic Disruptor UD-201 instrument. After the mixture was sonicated for 24 h (output = 5, active time with 0.5 s on, 0.5 s off), the insoluble carbon materials were isolated by filtration with membrane filters (Durapore HV, 0.45 μm). The solid was washed with toluene (50 mL) and diethyl ether (50 mL) and then dried under vacuum (0.04 Torr) at room temperature for 2 h to afford the Ru/CNF-P_{US} catalyst.

Characterization of the Ru Catalysts

ICP-MS: The Ru catalyst prepared as stated above (10 mg) was added to aqueous HCl (12 M, 10 mL). After the resultant suspension was heated at 70 °C for 20 h, the insoluble carbon materials were removed by filtration with membrane filters (Durapore HV, 0.45 μm). The supernatant obtained was diluted with aqueous HCl, and the concentration of HCl was adjusted to 5×10^{-3} wt%. The ruthenium content on the CNFs and AC was calibrated with a commercially available standard reagent (ACROS: ruthenium atomic absorption standard solution, 1 mg mL^{-1} Ru in 5% HCl); five standard solutions with Ru concentrations of 5–200 ppb were used for calibration.

TEM: One drop of a suspension of the Ru catalyst in *n*-butanol was deposited on the TEM grid (STEM 150 Cu grid, 150 μm), and the solvent was removed under reduced pressure (0.04 Torr) at room temperature. TEM observations were carried out with a JEOL JEM 2010F transmission electron microscope operating at 200 kV. Particle-size distributions were obtained from the TEM images with a digital camera.

XPS (Figure 3):[28] XPS spectra were obtained on a JEOL ESCA photoelectron spectrometer (JPS-900MC) with monochromated $Mg_{K\alpha}$ X-rays (10 kV, 10 mA). The base pressure in the spectrometer was typically 9.8×10^{-8} Torr. An ion beam was focused to about 0.5 cm^2 at normal incidence to the sample surface at gas pressures of about 10^{-5} Torr. Spectral deconvolutions of Ru $3d_{5/2}$ peaks for Ru^0 and Ru^{IV} were performed with Gaussian peak shapes by using an XPS peak-fitting program (XPSPEAK Version 4.1). Peak features such as peak positions and full widths at half maximum were checked on well-characterized samples (Ru powder 45 μm: 279.8 eV, RuO_2: 280.5 eV; purchased from WAKO Pure Chemical Ind., Ltd.) before any deconvolution of materials was attempted.

Hydrogenation of Aromatic Compounds

Hydrogenation of toluene was performed in a 100-mL stainless-steel autoclave fitted with a glass inner tube in the presence of substrate and ruthenium catalyst (5 mg) under H_2. The chemical yield and purity of the product were determined by capillary GLC analysis with *n*-octane or *n*-dodecane as an internal standard.

Table 4, entry 1: TC-17 (30 m), detection FID, column temperature 70 °C, $t_R = 4.3$ (methylcyclohexane), 4.7 (*n*-octane), 5.7 min (toluene).

Table 4, entry 2: TC-17 (30 m), detection FID, column temperature 100 °C, $t_R = 3.9$ (*n*-octane), 16.7 (ethyl cyclohexanecarboxylate), 26.2 min (ethyl benzoate).

Table 4, entry 3: TC-WAX (30 m), detection FID, column temperature 130 °C, $t_R = 4.5$ (*n*-dodecane), 7.8 (*cis*-ethyl 4-methylcyclohexanecarboxylate), 8.1 (*trans*-ethyl 4-methylcyclohexanecarboxylate), 23.1 min (*p*-toluic acid ethyl ester).

Table 4, entry 4: TC-17 (30 m), detection FID, column temperature 100 °C, $t_R = 3.9$ (*n*-octane), 5.3 (cyclohexyl methyl ether), 7.5 min (anisole).

Table 4, entry 5: The chemical yield and purity of the dicyclohexyl ether formed were determined by ^{1}H NMR spectroscopic analysis. Dicyclohexyl ether: ^{1}H NMR (396 MHz, $CDCl_3$): $\delta = 1.05$–1.64 (m, 12 H), 1.66–1.80 (m, 4 H), 1.81–1.95 (m, 4 H), 3.32 ppm (br s, 2 H). Diphenyl ether: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 6.99$–7.07 (m, 4 H), 7.07–7.18 (m, 2 H), 7.30–7.40 ppm (m, 4 H).

Table 4, entry 6: The chemical yield and purity of the cyclohexylamine formed were determined by ^{1}H NMR spectroscopic analysis. Cyclohexylamine: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 0.92$–1.42 (m, 7 H), 1.51–1.96 (m, 5 H), 2.62 ppm (tt, $J = 10.6$, 3.6 Hz, 1 H). Aniline: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 3.64$ (br s, 2 H), 6.69 (d, $J = 8.2$ Hz, 2 H), 6.76 (t, $J = 7.6$ Hz, 2 H), 7.16 ppm (dd, $J = 8.2$, 7.6 Hz, 2 H).

Table 4, entry 7: The chemical yield and purity of the *N,N*-dimethylcyclohexylamine formed were determined by ^{1}H NMR spectroscopic analysis. *N,N*-dimethylcyclohexylamine: ^{1}H NMR (396 MHz, $CDCl_3$): $\delta = 0.99$–1.39 (m, 5 H), 1.56–1.67 (m, 1 H), 1.69–1.97 (m, 4 H), 2.07–2.18 (m, 1 H), 2.27 ppm (s, 6 H). *N,N*-dimethylaniline: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 2.95$ (s, 6 H), 6.72 (t, $J = 6.8$ Hz, 1 H), 6.75 (d, $J = 8.2$ Hz, 2 H), 7.25 ppm (dd, $J = 8.2$, 6.8 Hz, 2 H).

Table 4, entry 8: The chemical yield and purity of the piperidine formed were determined by ^{1}H NMR spectroscopic analysis. Piperidine: ^{1}H NMR (396 MHz, $CDCl_3$): $\delta = 1.28$–1.51 (m, 7 H), 2.69 ppm (br s, 4 H). Pyridine: ^{1}H NMR (396 MHz, $CDCl_3$): $\delta = 7.28$ (dd, $J = 7.7$, 5.8 Hz, 2 H), 7.68 (tt, $J = 7.7$, 1.9 Hz, 1 H), 8.62 ppm (dd, $J = 5.8$, 1.9 Hz, 2 H).

Table 4, entry 9: SUPELCO β-DEX 120 (30 m), detection FID, column temperature 120 °C, $t_R = 15.0$ (cyclohexylmethyl alcohol), 21.2 ((*R*)-1-phenylethanol), 21.9 min ((*S*)-1-phenylethanol). The optical purity of the cyclohexylethyl alcohol formed was determined after conversion into the acetate: $t_R = 18.6$ (S isomer), 19.2 min (R isomer).

Table 4, entry 10: The chemical yield of the cyclohexylethylamine formed was determined by ^{1}H NMR spectroscopic analysis. Cyclohexylethylamine: ^{1}H NMR (396 MHz, $CDCl_3$): $\delta = 0.87$–1.05 (m, 2H), 1.02 (d, $J=$ 6.8 Hz, 3H), 1.05–1.29 (m, 6H), 1.61–1.87 (m, 5H), 2.65 ppm (qd, $J=6.8$, 6.3 Hz, 1H). 1-Phenylethylamine: ^{1}H NMR (396 MHz, $CDCl_3$): $\delta = 1.39$ (d, $J=6.8$ Hz, 3H), 1.46 (br s, 2H), 4.42 (q, $J=6.8$ Hz, 1H), 7.20–7.38 ppm (m, 5H). The optical purity of the 1-cyclohexylethylamine formed was determined after conversion into the acetamide: SUPELCO β-DEX 325 (30 m), detection FID, column temperature 135 °C, $t_R = 53.8$ (S isomer), 55.1 min (R isomer).

Hydrogenation of Toluene under Ambient Conditions

Preactivated Ru/CNF-P catalyst was generated by hydrogenation of 1-octene (350 mg) with Ru/CNF-P (5 mg) at 40 °C for 1 h under H_2 (initial pressure = 30 atm). Hydrogenation of toluene (1 mL) was then performed with preactivated Ru/CNF-P at ambient temperature for 18 h under H_2 (balloon) to afford methylcyclohexane in 9 % yield.

Biphasic Hydrogenation of Toluene with PEG-1000 as a Solvent

Table 5: Hydrogenation of toluene was performed in a 100-mL stainless-steel autoclave fitted with a glass inner tube in the presence of toluene (1 mL), PEG-1000 (100 mg), and Ru/CNF-P catalyst (10 mg) at 100 °C for 5 h under H_2 (initial pressure = 30 atm). Cooling of the reaction mixture to ambient temperature led to precipitation of solid PEG containing Ru/CNF-P catalyst. The product was separated by decantation, and its chemical yield and purity were determined by capillary GLC analysis with *n*-octane as an internal standard.

Biphasic Hydrogenation of (R)-1-Phenylethylamine with PEG-200 as a Solvent

Table 6, entry 8: Hydrogenation of (R)-1-phenylethylamine was performed in a 100-mL stainless-steel autoclave fitted with a glass inner tube in the presence of (R)-1-phenylethylamine (1 mL), PEG-200 (1 mL), and Ru/CNF-P catalyst (5 mg) at 100 °C for 24 h under H_2 (initial pressure = 30 atm). Addition of *n*-hexane (10 mL) to the reaction mixture led to phase separation; the upper phase was 1-cyclohexylethyamine in *n*-hexane, whereas the lower phase was liquid PEG-200 containing Ru/CNF-P catalyst. The upper phase was separated, and the residual PEG/catalyst phase was washed two times with *n*-hexane (total 20 mL). The combined organic phases were evaporated under reduced pressure to afford 1-cyclohexylethylamine in 70 % yield. The purity of the product was determined by capillary GLC analysis (> 99.9 % *ee*, *R*).

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