Highly-dispersed and Size-controlled Ruthenium Nanoparticles on Carbon Nanofibers: Preparation, Characterization, and Catalysis

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Facile synthesis of ruthenium nanoparticles supported on the carbon nanofibers (CNFs) is accomplished by thermal decomposition of $Ru_3(CO)_{12}$; ruthenium species on the platelet-type CNF are dispersed homogeneously and selectively on the edge of the graphite layers with narrow size distributions and behaves as an excellent catalyst for arene hydrogenation.

Recent progress of transition metal-immobilized materials for heterogeneous catalysis has provided a variety of interesting aspects for nano-sized metal particles on the nano-level-controlled solid supports.[1] Activated carbon (AC) has been the support of choice for metal-anchoring,[1a] however, there still remain drawbacks which should be improved; e.g. less-reproducibility for the catalyst performances and the deactivation of the catalyst by sintering and/or leaching of the metallic species. These drawbacks can be attributed to ill-controlled structures of AC having a wide variety of surface and pore structures. In this context, carbon nanofibers (CNFs) having well-controlled nano-structures could be attractive catalyst supports, if metal nanoparticles are highly dispersed on the surface of CNFs. The CNFs are classified into three types: Graphite layers are parpendicular (platelet: CNF-P), parallel (tubular: CNF-T), and stacked obliquely (herringbone: CNF-H).[2] We have recently reported selective synthesis of these three types of CNFs in large scales.[3] The CNF-supported catalysts[4] are reportedly prepared by the incipient wetness method to immobilize metal salts on the surface; however, it is necessary to perform subsequent reduction of the metal salts with H_2 at high temperature, and the process sometimes causes aggregation of the metallic species.[5] This means that effective methods for anchoring size-controlled metal particles on the CNFs is an important research project to be explored. We wish to report here a method for the Ru nanoparticles on the CNFs (Ru/CNFs) using $Ru_3(CO)_{12}$ as a zero-valent organometallic precursor;[6] the reaction with CNF-P is particularly important leading to highly-dispersed and size-controlled Ru nanoparticles on the surface. Although $Ru_3(CO)_{12}$ is well known to react facilely with polyaromatic hydrocarbons such as acenaphthylene derivatives,[7a] fullerenes, and graphite,[7b] there has been no precedence for the reaction with CNFs.

The Ru/CNFs catalysts were readily prepared by thermal decomposition of $Ru_3(CO)_{12}$ in refluxing toluene in the presence of CNFs under an argon atmosphere (see Electronic Supporting Information; ESI). For comparison, we also immobilized Ru species on AC (Ru/AC) by the same method. The inductively coupled plasma-mass (ICP–MS) analysis revealed that 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 %). In contrast, that of the others was not reproducible, and was dependent on each sample (1.1–3.8 wt % for Ru/CNF-T and 1.1–1.6 wt % for Ru/CNF-H). The TEM images of these carbon materials showed the size distribution and the location of nanoparticles are highly dependent on the structure of carbon materials. The photo of the Ru/CNF-P is especially of interest, revealing that small and spheroidal species ($d_{av} = 2.5$ nm) are homogeneously dispersed selectively on the edge of the graphite layers[8] (Figure 1). This is in sharp contrast to the TEM images of the Ru/CNF-T and Ru/CNF-H, in which coexistence of some large Ru masses ($10 < d < 50$ nm for Ru/CNF-T and $50 < d < 150$ nm for Ru/CNF-H, respectively) and small particles (<4.5 nm). The small species on CNF-T are located both in the tubes and on the surface, whereas nano particles were found between the graphite layers and on the surface for Ru/CNF-H[9] (see ESI). Existence of dispersed nanoparticles is observed in the photo of Ru/AC; however, a majority of the Ru particles is located inside the pores ($d = 1.5$–4.0 nm). The formation of the large ruthenium masses in Ru/CNF-T and Ru/CNF-H may relate to non-reproducibility of the ruthenium content in their production as described above. The XPS survey spectra of these Ru catalysts displayed close two Ru $^3d_{5/2}$ signals assignable to the zero-valent ruthenium and oxidized RuO_2; a characteristic feature of the Ru/CNF-P is that the high contents of the Ru^0 species existed on the surface ($Ru^0/Ru^{IV} = 74{:}26$).[10] Thus, the present method allowed an important discovery that the CNF-P is the most effective for anchoring highly-dispersed ruthenium nanoparticles of narrow size on the carbon surface with high contents of Ru^0 species. Since the hydrogenation is known to proceed efficiently by an active zero-valent metal catalyst with large surface area (i.e., small size metal particles) located on the surface, the Ru/CNF-P is expected to act as efficient hydrogenation catalyst.

Indeed, high catalytic activity of the Ru/CNF-P was verified in the hydrogenation of toluene (Table 1). First, the Ru/CNF-P smoothly catalyzed the reduction of toluene to afford methylcyclohexane as the sole product in quantitative yield without any induction period (Entry 1). The chemical yield of the product was reproducible over ten different experiments. In sharp contrast, the conversion of toluene was different in each experiment

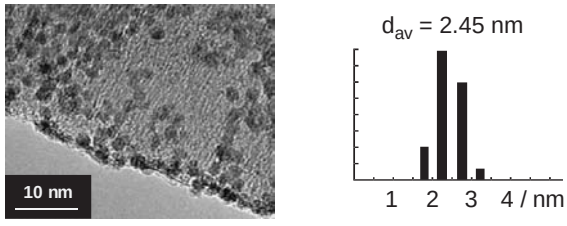


Figure 1. TEM image and histogram of the Ru particles on CNF-P.

Table 1. Hydrogenation of toluene catalyzed by Ru catalysts[a]

Entry	Catalyst	Conditions	Conversion/%[b]
1	Ru/CNF-P	100 °C, 2.5 h	>99
2	Ru/CNF-T	100 °C, 5 h	3–99[c]
3	Ru/CNF-H	100 °C, 5 h	0–99[c]
4	Ru/AC	100 °C, 5 h	3–90[c]
5[d]	Ru/CNF-P	40 °C, 1 h	89–94
6[d]	Ru/CNF-T	40 °C, 1 h	<1
7[d]	Ru/CNF-H	40 °C, 1 h	9–24[c]
8[d]	Ru/AC	40 °C, 1 h	<1
9[d]	Ru/C (5 wt %)[e]	40 °C, 1 h	<1

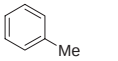
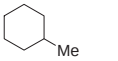
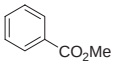
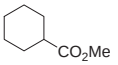
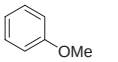
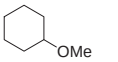
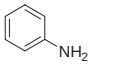
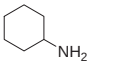
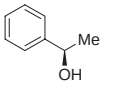
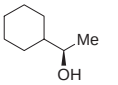
[a]All reactions were carried out using 3 mL of toluene, 5 mg of ruthenium catalyst under H_2 (30 atm). [b]Determined by capillary GLC analysis. [c]A small amount of methylcyclohexene was formed. [d]1 mL of toluene was used. [e]Purchased from N.E.CHEMCAT.

catalyzed by three other catalysts (Entries 2–4). Excellent catalytic activity of Ru/CNF-P was also seen in the reaction at lower temperature (Entries 5–9). The Ru/CNF-P catalyst was used for five cycles of reaction without loss of catalytic activity. ICP-MS analysis of the product obtained by the recycle experiments revealed that there was no detectable amount of Ru species.[11] In addition, the TEM image of the Ru/CNF-P catalyst after the fifth run showed some aggregation of Ru species, but the average diameter of Ru particles was still kept bellow 3 nm with narrow size distributions. These results clearly showed that the CNF-P captures the catalytically active Ru nanoparticles tightly on its surface, and high catalytic activity and efficiency of the Ru/CNF-P can be achieved in the hydrogenation.

The Ru/CNF-P catalyst also showed high catalytic efficiency for the functionalized benzene derivatives with excellent chemoselectivity (Table 2). It is well known that the reactivity of the aromatic compounds with heteroatom-containing substituents, especially benzoate and aniline, are lower than those of benzene or toluene;[12] however, the TOFs are often comparable to the Pd/SiO_2-immobilized Rh complex, which is the most efficient catalyst reported by Angelici et al.,[13] and even higher in some cases. In the reduction of benzoate, neither hydrogenolysis product nor the product formed from the reduction of the carbonyl group was detected (Entry 2). Similarly, the optically active (*R*)-1-phenylethyl alcohol is a good substrate to check the possible epimerization and hydrogenolysis of the benzylic C–O bond during the hydrogenation; however, exclusive formation of (*R*)-1-cyclohexylethyl alcohol (>99% ee) in quantitative yield completely ruled out this possibility (Entry 5).

In summary, we have succeeded in facile immobilization of ruthenium nanoparticles on the three types of CNFs via thermal decomposition of organometallic precursor $Ru_3(CO)_{12}$; the location of Ru nanoparticles is attributed to the fine structures of 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 surface (CNF-H). Of particular interest is highly-dispersed and size-controlled ruthenium nanoparticles on the surface of Ru/CNF-P, which shows high and reproducible catalytic activity and chemoselectivity in the arene hydrogenation; the reactions proceed without sintering and leaching of the Ru species, and the catalyst can be recycled without loss of the activity. The combination of two "nanotechnology," i.e., nano-sized metal particles and the nano-level-controlled solid support, first makes possible to achieve such catalyst properties. We are currently investigating the electronic properties of Ru/CNFs and application

Table 2. Reduction of various aromatic compounds by Ru/CNF-P[a]

Entry	Substrate	Time /h	Product	Yield /%[b]	TON[c] [TOF][d]
1[e]		2.5		>99	35800 [14300]
2		5		>99	8500 [1700]
3		5		>99	11600 [2300]
4		24		>99[f]	13900 [600]
5[g]		3		>99	5250 [1750]

[a]All reactions were carried out using 1 mL of substrate, 5 mg of Ru/CNF-P at 100 °C under H_2 (30 atm). [b]Determined by capillary GLC analysis. [c]TON = mol (substrate)/mol (Ru). [d]TOF = mol (substrate)/mol (Ru)·h. [e]3 mL of toluene was used. [f]Determined by ^{1}H NMR analysis. [g]0.5 mL of substrate was used under H_2 (20 atm).

of this synthetic method using zero-valent organometallic precursors to other transition metal-immobilized CNF catalysts.

The authors acknowledge the financial support from CREST-JST (Japan Science and Technology Corporation). Help for TEM and XPS analysis by Dr. Seongyop Lim and Sang-Min Jang, Institute for Materials Chemistry and Engineering, Kyushu University, is acknowledged.

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Published on the web (Advance View) July 1, 2006; doi:10.1246/cl.2006.876