

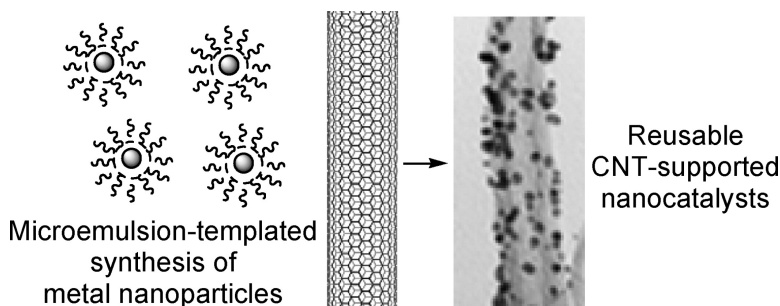
Communication

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Microemulsion-Templated Synthesis of Carbon Nanotube-Supported Pd and Rh Nanoparticles for Catalytic Applications

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Palladium nanoparticles stabilized and dispersed by water-in-oil microemulsions are very active catalysts for hydrogenation of olefins in organic solvents.¹ However, recycling nanoparticle catalysts stabilized in water-in-oil microemulsions is experimentally difficult. Carbon nanotubes (CNTs), due to their unusual properties, are promising carbonaceous materials for supporting catalytic nanoparticles.² Because of their small sizes, CNT-supported catalytic nanoparticles can be uniformly dispersed in organic solvents by stirring. Recycling CNT-supported catalytic nanoparticles can be accomplished by gravitational sedimentation. Known methods for depositing catalytic nanoparticles on CNTs including supercritical fluid, solid-state, or aqueous reactions usually require high temperatures or pressures.³ Water-in-oil microemulsions have been used as templates for synthesizing nanoparticles. Ingelsten et al. reported a method of depositing Pt nanoparticles synthesized in a water-in-oil microemulsion on alumina.⁴ The microemulsion was destabilized by adding tetrahydrofuran to release the metal nanoparticles for deposition. The process was slow, and agglomeration of the Pt nanoparticles occurred during the deposition. Hanaoka et al. also used a water-in-oil microemulsion to synthesize Rh nanoparticles by hydrogen reduction and followed this step by depositing them on silica.⁵ There is no report in the literature regarding microemulsion-templated deposition of metal nanoparticles on CNT surfaces. The feasibility of using a water-in-oil microemulsion for synthesizing Pd and Rh nanoparticles followed by their direct deposition on CNT surfaces was investigated recently in our laboratory. This simple approach turns out to be very effective for making CNT-supported catalytic metal nanoparticles that are uniformly anchored on CNT surfaces with a narrow size distribution. The synthetic process can be carried out at room temperature and requires only water-soluble metal salts as starting materials. Hydrogen gas can be used as a reducing agent to convert Pd²⁺ and Rh³⁺ ions to their elemental states leading to nanoparticles formation within the microemulsion.¹ Deposition of metal nanoparticles on CNT surfaces is achieved by stirring CNTs in the microemulsion solution. This method of making CNT-supported nanoparticles, including monometallic, bimetallic, or even multimetallic ones, provides a simple way of studying a variety of nanoscale metal catalysts of different compositions.

The functionalized multiwalled carbon nanotubes (fMWCNTs) were prepared by a method known in the literature.⁶ Formation of metal nanoparticles in a water-in-hexane microemulsion using sodium bis(2-hexylethyl)sulfosuccinate (AOT) as the surfactant and hydrogen gas as the reducing agent was described in a previous article.¹ The fMWCNTs were added to the water-in-hexane microemulsion solution, and the metal nanoparticles formed in the microemulsion could be transferred to the CNT surfaces in 30 min of stirring. Transmission electron microscope (TEM) images of the Pd, Rh, and Pd/Rh nanoparticles deposited on the surfaces of the fMWCNTs are shown in panels a, b, and c of Figure 1, respectively.

The Pd and Rh nanoparticles deposited on the fMWCNTs have size distributions in the range of about 2–10 nm and are dispersed

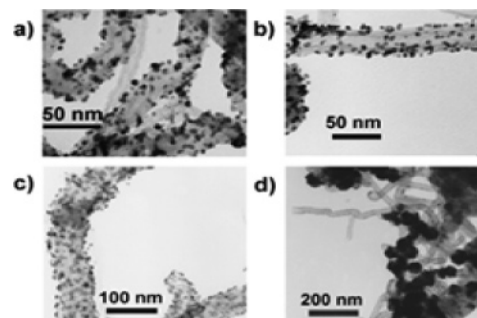


Figure 1. TEM images of the microemulsion-templated synthesis of CNT-supported metal nanoparticles: (a) Pd/CNTs, (b) Rh/CNTs, (c) Pd/Rh bimetallic nanoparticles from the microemulsion methods, and (d) Pd/CNTs from an aqueous Na₂PdCl₄ solution.

on the substrate surfaces. Without the microemulsion, direct deposition of Pd or Rh on the fMWCNTs by hydrogen reduction of an aqueous Na₂PdCl₄ or RhCl₃ solution, respectively, resulted in metal particles about 1 order of magnitude larger and clumped together as shown in Figure 1d. This result was also observed when a palladium(II) hexafluoroacetylacetonate [Pd(hfa)₂] was reduced in hexane with hydrogen in the presence of the fMWCNTs. The TEM images demonstrate that the microemulsions are responsible for making metal nanoparticles on the surfaces of the fMWCNTs. The nanoparticles also could not be induced by the TEM beam because virtually no Rh nanoparticles were observed after exposing Rh³⁺ soaked fMWCNTs in our TEM.⁷

In X-ray photoelectron spectroscopy (XPS) analyses of the CNT-supported metal nanoparticles, 12.69 wt % of Pd and 17.33 wt % of Rh were found in the Pd/CNT and in the Rh/CNT catalyst, respectively. On the basis of the amounts of the metal salts used in the preparation of the microemulsion, we estimated that about 43% of palladium from Na₂PdCl₄ and 58% of rhodium from RhCl₃ were deposited as metallic nanoparticles on the surfaces of the fMWCNTs in the synthetic process. Repeated washing with methanol 5 times to remove the AOT from the CNT-supported metal nanoparticles was required to purify the nanoparticles. After the washing, no sulfur peak was detected in the CNT-supported nanoparticle samples by energy-dispersive X-ray spectroscopy (EDX) and XPS. The asymmetric and symmetric stretching of the SO₂ group of the AOT was also not detected in the CNT samples by FT-IR. After 10 repeated uses of the catalyst for hydrogenation of *trans*-stilbene as in eq 1, TEM images showed little change in the distribution and size of the Pd nanoparticles deposited on the CNT surfaces and the catalyst did not show detectable loss of activity. An X-ray diffraction (XRD) pattern of the CNT-supported Pd catalyst (given in the Supporting Information) revealed the Pd(111) peak at $2\theta = 40.20 \pm 0.05^\circ$, and the Rh/CNT catalyst showed the Rh(111) peak at $2\theta = 41.15 \pm 0.05^\circ$, consistent with the metallic Pd and Rh data in the literature.

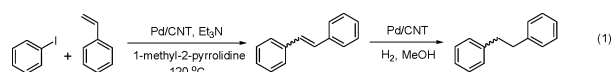

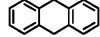
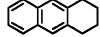



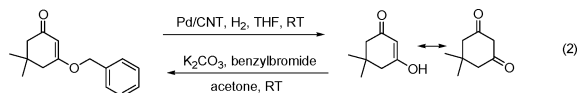
Table 1. Catalytic Hydrogenation of Anthracene Using CNT-Supported Nanocatalysts

Catalyst				
Rh/C ^a	>99 %	ND	ND	ND
Rh/CNT ^b	23.8 %	4.1 %	62.4 %	9.7 %
Pd/CNT ^b	19.1 %	80.9 %	ND	ND
Pd-Rh/CNT ^{b,c}	ND	7.3 %	ND	92.7 %

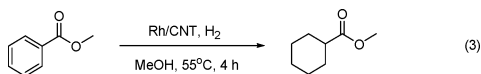
^a 0.0300 g of 5 wt % Rh. ^b 0.0100 g of the CNT-supported metal nanoparticles. ^c 6.3 wt % Pd and 6.9 wt % Rh. All catalysts were used after drying in the oven for 1 h at 100 °C, and stirring speed was optimized at 600 rpm. Anthracene (0.0178 g, 0.1 mmol) with the nanocatalyst was stirred for 30 min under 10 atm of H₂ pressure in methanol at 25 °C. The conversion yield was determined by NMR and HPLC (C₁₈ column, MeOH/H₂O = 4:1). ND = not detectable.

To test activities of the CNT-supported Pd nanoparticles, iodobenzene and styrene were selected for the Heck coupling reaction. The coupling product was obtained with 94% of the isolated yield after 3 h of the reaction shown in eq 1. A conventional palladium/carbon catalyst (10 wt % Pd from Aldrich) was also used for this coupling reaction under the same conditions, and the Heck coupling product (*trans*-stilbene) with 53% conversion yield was detected after 24 h. The particle size of the commercial Pd catalyst showed a very large variation, typically about 2 orders of magnitude larger than the CNT-supported nanoparticles. It was reported that the pore size, acid–base properties, and impurities of the conventional carbon supports could influence the metal particle distributions.⁸ The conversion of *trans*-stilbene to 1,2-diphenylethane was about 99% after 10 min of reaction using 1 atm of H₂ gas at 25 °C. Using the commercial Pd/C catalyst, it would require 1 h to achieve the same degree of hydrogenation of *trans*-stilbene under the same conditions. The high catalytic activity of the CNT-supported Pd nanoparticles in forming a new carbon–carbon bond via the Heck coupling is potentially significant for organic synthesis applications.

The debenzoylation of the protected group is conventionally carried out with Pd as a catalyst. To test the effectiveness of the Pd/CNT catalyst, we synthesized O-alkylated 5,5-dimethyl-1,3-cyclohexanedione derivatives as shown in eq 2.⁹ After 3 h using the Pd/CNT catalyst, the debenzoylation products were obtained with 95% of yield (eq 2). In case of the commercial Pd/C catalyst, less than 10% of the starting materials were converted to the debenzoylated products after 9 h of reaction under the same conditions. The CNT-supported Pd nanoparticles are obviously much more active than the commercial Pd/C catalyst for the debenzoylation process.



In another case, methyl benzoate in methanol was essentially all converted (>99%) to methyl cyclohexanecarboxylate after 4 h of reaction with the Rh/CNT nanoparticles under the conditions specified in eq 3.



A comparison of the catalytic activity between a commercial Rh/C (5 wt % of Rh from Strem Chemicals) catalyst and the Rh/CNT nanoparticles was made for hydrogenation of anthracene (Table 1). No conversion of anthracene was detected with the commercial Rh/C catalyst after 2 h of reaction at 25 °C with 10 atm of H₂. For the CNT-supported Rh nanoparticles, none of the

starting material anthracene was detected by TLC, NMR, and HPLC after 1 h of reaction under the same conditions.

An interesting observation is that when a mixture of Pd²⁺ and Rh³⁺ ions was used as the starting material in the water core of the microemulsion for the synthesis, the resulting Pd/Rh nanoparticles deposited on the fMWCNTs (Figure 1c) are more active than the single metal nanoparticles prepared in the same way for catalytic hydrogenation of anthracene. Using CNT-supported Pd or Rh monometallic nanoparticles, the conversion yield of anthracene to 1,2,3,4,5,6,7,8-octahydroanthracene was less than 10%. The corresponding product was obtained at 92.7% with CNT-supported Pd/Rh nanoparticles under the same conditions (Table 1). The CNT-supported Pd/Rh catalyst was found to contain 6.3 ± 0.1 wt % Pd and 6.9 ± 0.4 wt % Rh in EDX and XPS analyses. The XRD data showed a single peak for the Pd/Rh nanoparticles deposited on the fMWCNTs with a 2θ value between that of the Pd (2θ = 40.20°) and Rh (2θ = 41.15°) metal nanoparticles. XPS spectra of the Pd/Rh catalyst revealed the presence of Pd(3d_{5/2}) and Pd(3d_{3/2}) peaks at 335.4 and 340.7 eV, respectively, and Rh(3d_{5/2}) and Rh(3d_{3/2}) peaks at 307.2 and 311.9 eV, respectively.

According to a recent report, bimetallic nanoparticles may have a number of different morphologies that would not show changes in XPS spectra.¹⁰ The enhanced catalytic activity of the CNT-supported Pd/Rh bimetallic system could be due to certain arrangements of the Pd and Rh nanoclusters on the nanoparticles' surfaces. The Pd/Rh nanoparticles synthesized by the microemulsion method described in this communication are probably bimetallic in nature with an unknown morphology.

In conclusion, the fMWCNT-supported Pd, Rh, and Rh/Pd nanoparticle catalysts can be prepared easily with high yields using water-in-oil microemulsions containing metal ions as starting materials. Metal nanoparticles are formed by hydrogen reduction of metal ions in the water core with 1 atm H₂ gas at 25 °C. The CNT-supported Rh nanoparticles are active catalysts for hydrogenation of arenes, and the CNT-supported bimetallic Pd/Rh nanoparticles show an unusually high catalytic activity for hydrogenation of anthracene. This simple and novel synthetic technique for making CNT-supported monometallic and bimetallic nanoparticles may have a wide range of catalytic applications for chemical syntheses.

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Supporting Information Available: Experimental details and XRD data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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