Microemulsion-templated synthesis of carbon nanotube-supported Pd and Rh nanoparticles for catalytic applications

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Supporting Information

XRD Data

Figure 1. X-ray diffraction data collected at ambient temperature in transmission mode on a Siemens D5000 Diffractometer from the CNT-supported metal nanoparticles (Cu Kα1, Ge-monochromated, λ = 1.54056 Å, 2θ range, 10°-80°; step size, 0.02°; data collection time, 2 h): a) Pd/CNTs; b) Rh/CNTs; c) 4.7:5.3 ratio of Pd:Rh bimetallic/CNTs compared with literature values of Pd (111) at 2θ = 40.114 and Rh (111) at 2θ = 41.068; and d) enlarged profiles in a range of 2θ = 39.1-42.7.

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Experimental Section

The microemulsions were prepared at 25 °C by mixing 0.1 M of Na₂PdCl₄ or RhCl₃ aqueous solution (0.864 mL) with 200 mL of n-hexane and sodium dioctyl sulfosuccinate (AOT, 1.7782 g, 4 mmol) that gave a W value ([H₂O]/[surfactant]) of 12.¹ Multi-walled carbon nanotubes (1.0 g, 60-100 nm in diameter, Nanostructured & Amorphous Materials Inc, USA) were pretreated by sonication in 14 M HNO₃ for 1 h and then refluxed for 12 h in a mixture of HNO₃ (50 mL, 14 M) and H₂SO₄ (98 % 50 mL). The functionalized MWCNTs (0.030 g) were added to the microemulsion solution with continuous stirring. Hydrogen gas at 1 atm was then bubbled through the solution for 30 min to reduce the Pd²⁺ or Rh³⁺ ions dissolved in the water core of the microemulsion. It is known that hydrogen gas can cause reduction of Pd²⁺ or Rh³⁺ ions in aqueous solutions to their elemental states.¹ After hydrogen reduction, the CNT-supported metal nanoparticles would precipitate to the bottom of the flask without stirring. The hexane solution containing AOT was carefully removed and the surfactant AOT could be recovered later if needed. The CNT precipitates were washed with methanol several times and then dried in a hood.

The dry CNT precipitates were characterized by TEM (JEM-1200EX), scanning electron microscopy (SEM, AMRAY 1830 HITACHI S-2300) with EDX, XPS (KRATOS Analytical, AXIS-165), and XRD (Siemens, D5000). A FT-IR spectra was acquired with a Nicolet AVATAR 370 DTGS spectrometer that was purged with N₂. XPS data were taken with a monochromatized Al Ka at Pass Energy (PE) of 80 eV for the survey scan (energy resolution of 1.2 eV) and PE of 40 eV for the high resolution scans of Rh and Pd (energy resolution of 0.75 eV). The CNT-supported metal nanoparticles were also tested for their catalytic activities using hydrogenation reactions with olefins and arenes, carbon-carbon coupling, and carbon-oxygen cleavage reactions. A ¹H NMR (300 MHz, CDCl₃, Bruker, AMX300) and a HPLC (SpectraSYSTEM, SCM1000) with the UV absorption detector were used for organic product analysis. The conventional Pd/C (10 wt % of Pd) and Rh/C (5 wt % of Rh) catalysts were purchased from Sigma Aldrich and Strem Chemicals. All other chemicals and reagents were obtained from Sigma Aldrich.

The procedure for the CNT-supported Pd nanoparticles catalyzed Heck coupling reaction is given as follows. To a solution of the catalyst (0.010 g, 43 wt % of Pd) and triethylamine (0.076 g, 0.75 mmol) in 1-methyl-2-pyrrolidine (NMP, 5 mL) were added to iodobenzene (0.100 g, 0.5 mmol) and styrene (0.055 g, 0.53 mmol) and stirred for 5 min under nitrogen atmosphere. The reaction mixture was stirred for 3 h at 120 °C under nitrogen. After aqueous work up, the solvent was removed and the product was obtained with 94 % of isolated yield (0.085 g).

For the CNT-supported Rh nanoparticles catalyzed arene ring reduction, a stainless steel high pressure reactor (100 mL) was equipped with a magnetic bar and a temperature and pressure controller. The catalyst (0.030 g, 58 wt % of Rh) was added to a solution of methyl benzoate (0.865 g, 6.4 mmol) in dry methanol. The reaction mixture was stirred for 4 h under 10 atm of hydrogen at 55 °C. After the reaction, the CNT-supported metal catalyst would slowly settle down to the bottom of the reaction vessel. By carefully removing the methanol solution, the catalyst can be recovered and washed with alcohol for repeated use. For the commercial Pd/C and Rh/C catalysts experiments, equivalent amounts of the metal catalysts were used for comparison with the CNT-supported metal nanocatalysts. The analytical data for all products were satisfactorily matched with their values in the literature.