Supporting Information

Palladium Nanoparticles Supported onto Ionic Carbon Nanotubes as Robust Recyclable Catalysts in Ionic Liquids

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Materials: Multiwalled Carbon Nanotubes (MWCNT) was purchased from Iljin Nanotech Co., Ltd (purity: >95%, length: 10–50 um, diameter: 10–30 nm). The imidazolium bromide-functionalized multi-walled carbon nanotubes 1 (IL-f-MWCNT) were prepared according our reported procedure.1 Ionic liquids contained less than 10 ppm of chlorine in chlorine analysis at Analysis Center in Korea Institute of Science and Technology and less than 15 ppm of water in Karl Fischer analysis (Metrohm Model: 756KF Coulometer). All other chemicals were commercial available and used without further purification. All reagents were used as received, and all solvents were distilled prior to use.

Measurements: High Resolution Transmission Electron Microscope (HR-TEM) analyses were conducted with JEM-3010 (JEOL, 300Kv) at National center for inter-university research facilities in Seoul National University. X-Ray Photoelectron Spectrometer (XPS) measurements were performed with ESCALAB 250 XPS spectrometer at Korea Basic Science Institute Busan Center. Powder X-ray diffraction (XRD) patterns were measured with a Philips PW 1830 diffractometer with Ni-filtered Cu Kα radiation (λ = 1.5418 Å) from the thin film of the samples deposited on glass substrate. Inductive coupled plasma atomic emission spectrometer (ICP-AES) analyses were conducted with Perkin Elmer (Optima-4300DV).

Synthesis of Palladium Nanoparticles-Supported onto Imidazolium Bromide-functionalized Multi-walled carbon nanotubes [Pd/IL-f-MWCNT(Br)] (2a): To an aqueous solution of imidazolium bromide-functionalized multi-walled carbon nanotube, IL-f-MWCNT 1 (178.0 mg) in H2O (200 mL) was added Na2PdCl4 (800.0 mg), and the mixture was stirred vigorously for 30 min under 1 atm of H2 (ballon) at room temperature. The resulting black Pd/IL-f-MWCNT 2a having bromide anion was filtered through a 0.2-µm Millipore® polycarbonate membrane, and washed successively with deionized water and methanol several times. The filtered black solid was dried under vacuum for 24 h at room temperature to give 2a (435.0 mg, 58.3 wt% of Pd).

Synthesis of [Pd/IL-f-MWCNT(NTf2)] (2b) and [Pd/IL-f-MWCNT(SbF6)] (2c): An aqueous solution of the Pd/IL-f-MWCNT having Br anion (2a, 220 mg, 58 wt % of Pd) in deionized water

(80 mL) was sonicated for 30 min, and then lithium bistrifluoromethansulfonimidate (LiNTf$_2$) (287 mg, 1 mmol) was added. The reaction mixture was stirred at room temperature for 12 h, and the black solid was filtered through a 0.2-μm Millipore® polycarbonate membrane. The filtrate was washed successively with deionized water and methanol several times. The filtered black solid was dried under vacuum for 24 h at room temperature to give Pd/IL-f-MWCNT 2b having NTf$_2$ anion (219 mg, 55.2 wt % of Pd). The Pd/IL-f-MWCNT 2c having SbF$_6$ anion was synthesized as described above, the Pd/IL-f-MWCNT 2a (232 mg) was converted to give Pd/IL-f-MWCNT 2c (230 mg, 54.4 wt % of Pd) via anion exchange.

A typical procedure for the hydrogenation using Pd/IL-f-MWCNTs 2. To a suspension solution of the catalyst Pd/IL-f-MWCNT 2c (1.8 mg, 1.0 mol % based on Pd content) in a solvent [iPrOH (10 mL), MeOH (10 mL), MeOH/[bmim][NTf$_2$] (8.0 mL/2.0 mL), MeOH/[bmim][SbF$_6$] (8.0 mL/2.0 mL)] was added trans-stilbene (180.0 mg, 1.0 mmol), and the reaction mixture was stirred vigorously under 1 atm of H$_2$ (balloon) at room temperature. Completion of the conversion was determined by GC analysis. The results are in Table 1. For recycling experiments, the same hydrogenation was conducted using Pd/IL-f-MWCNTs 2c in iPrOH/[bmim][SbF$_6$]. After completion the reaction by GC analysis, the upper iPrOH layer was separated, and ionic liquid layer was extracted with iPrOH (5 mL x 2 times). The combined iPrOH was concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel (Merck 60, 230-400 mesh) (or by distillation) to give hydrogenated product, 1,2-diphenylethane (178 mg, 98 %). The recovered Pd/IL-f-MWCNT 2c/[bmim][SbF$_6$] was reused for the next run by addition of fresh iPrOH and substrate. Leaching of tiny amount of [bmim][SbF$_6$] into iPrOH has been observed, and 0.3 mL of [bmim][SbF$_6$] was additionally added after every 20 times reusing. The results are listed in Table 2. For characterization of the hydrogenated compounds, after evaporation of iPrOH, the residue was purified by silica-column chromatography.

1,2-diphenylethane: GC condition: 200 °C isothermal; Retention time: 1,2-diphenylethane (3.0 min), stilbene (4.35 min); $^1$H NMR (CDCl$_3$, 250 MHz) δ 7.33-7.38 (m, 4H), 7.23-7.30 (m, 6H), 3.00 (s, 4H) ppm; $^{13}$C NMR (CDCl$_3$, 63 MHz) δ 141.9, 128.6, 128.4, 126.0, 38.1 ppm.

Ethylbenzene: GC odcondition: 120 °C isothermal; Retention time: ethylbenzene (2.35 min), styrene (2.47 min); $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.45-7.0 (m, 5H), 2.63 (q, $J = 7.6$ Hz, 2H), 1.22 (t, $J = 7.6$ Hz, 3H) ppm; $^{13}$C NMR (CDCl$_3$, 63 MHz) δ 144.2, 128.4, 127.9, 125.7, 28.9, 15.6 ppm.

Propylbenzene: GC condition: 140 °C isothermal; Retention time: propylbenzene (2.28 min), β-methylstyrene (2.54 min); $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.4-7.0 (m, 5H), 2.58 (t, $J = 7.4$ Hz, 2H), 1.89-1.60 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 63 MHz) δ 143.7, 128.5, 128.3, 125.7, 38.09, 23.7, 14.1 ppm.

2-Methylpropylbenzene: GC condition: 130 °C isothermal; Retention time: 2-methylpropyl benzene (2.71 min), 2-methyl-1-phenylpropene (3.18 min); $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.29-7.11 (m, 5H), 2.46 (d, $J = 7.2$ Hz, 2H), 1.86 (m, 1H), 0.9 (d, $J = 6.6$ Hz, 6H) ppm; $^{13}$C NMR (CDCl$_3$, 63 MHz) δ 141.7, 129.2, 128.1, 125.7, 45.6, 30.3, 22.5 ppm.

Methyl 3-phenylpropionate: GC condition: 180 °C isothermal; Retention time: Methyl 3-
phenylpropionate (2.50 min), trans-methyl cinnamate (3.02 min); $^1$H NMR (CDCl$_3$, 250 MHz) δ 7.30-7.26 (m, 2H), 7.22-7.18 (m, 3H), 3.66 (s, 3H), 2.95 (t, $J$ = 8.6 Hz, 2H), 2.63 (t, $J$ = 8.2 Hz, 2H) ppm; $^{13}$C NMR (CDCl$_3$, 63 MHz) δ 173.5, 140.7, 128.7, 128.4, 128.5, 52.0, 36.1, 31.4 ppm.

(4-Chlorophenyl)ethane: GC condition: 130 °C isothermal; Retention time: 1-Chloro-4-ethylbenzene (3.04 min), 4-chlorostyrene (3.20 min); $^1$H NMR (CDCl$_3$, 250 MHz) δ 7.23 (d, $J$ = 8.1 Hz, 2H), 6.83 (d, $J$ = 8.6 Hz, 2H), 3.78 (s, 3H), 2.59 (q, $J$ = 7.6 Hz, 2H), 1.20 (t, $J$ = 7.6 Hz, 3H) ppm; $^{13}$C NMR (CDCl$_3$, 63 MHz) δ 159.5, 136.4, 128.7, 113.7, 55.3, 28.0, 15.9 ppm.

(4-Methoxyphenyl)ethane: GC condition: 160 °C isothermal; Retention time: (4-methoxyphenyl)ethane (2.39 min), 4-vinylanisole (2.55 min); $^1$H NMR (CDCl$_3$, 250 MHz) δ 7.53 (d, $J$ = 8.1 Hz, 2H), 7.30 (d, $J$ = 7.9 Hz, 2H), 2.71 (q, $J$ = 7.5 Hz, 2H), 1.26 (t, $J$ = 7.5 Hz, 2H) ppm; $^{13}$C NMR (CDCl$_3$, 63 MHz) δ 143.9, 128.1, 125.2, 28.8, 15.3 ppm.

(4-(Trifluoromethyl)phenyl)ethane: GC condition: 105 °C isothermal; Retention time: (4-(trifluoromethyl)phenyl)ethane (2.87 min), 4-(trifluoromethyl)-styrene (2.98 min); $^1$H NMR (CDCl$_3$, 250 MHz) δ 7.53 (d, $J$ = 8.1 Hz, 2H), 7.30 (d, $J$ = 7.9 Hz, 2H), 2.71 (q, $J$ = 7.5 Hz, 2H), 1.26 (t, $J$ = 7.5 Hz, 2H) ppm; $^{13}$C NMR (CDCl$_3$, 63 MHz) δ 165.55, 146.99, 124.69, 28.83, 14.48 ppm.

We also attempted to deposit Pd nanoparticles using IL-f-MWCNTs having hydrophobic NTf$_2$ anion. However, as shown in Figure S2, the palladium nanoparticles are deposited onto the only limited CNTs, which may largely due to the insolubility of the hydrophobic IL-f-MWCNTs having NTf$_2$ anion. However, the size distributions are similar with that of the Pd/IL-f-MWCNTs 2a having hydrophilic Br anion.

![Figure S1](image)

**Figure S1.** TEM images of the Pd/IL-f-MWCNTs 2b (a) prepared by hydrogen reduction of Na$_2$PdCl$_4$ in H$_2$O using IL-f-MWCNTs having hydrophobic NTf$_2$ anion (scale bar: 100nm, inset scale bar: 20 nm), (b) prepared by anion exchange of 2a with LiNTf$_2$ in H$_2$O (scale bar: 20 nm).
Figure S2. X-ray photoelectron spectroscopy (XPS) of Pd/IL-f-MWCNT 2a having Br anion. (a) wide scan, (b) Pd(3d) region, (c) Br(3d) region.

Figure S3. X-ray photoelectron spectroscopy (XPS) of Pd/IL-f-MWCNT 2b having NTf₂ anion: (a) wide scan, (b) Pd(3d) region, (c) F(1s) region.
Figure S4. X-ray photoelectron spectroscopy (XPS) of Pd/IL-f-MWCNT 2c having SbF₆ anion. (a) wide scan, (b) Pd(3d) region, (c) F (1s) region (d) Br (3d) region

Figure S5. XRD of Pd/IL-f-MWCNT (a) 2a, (b) 2b, and (c) 2c