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Supporting Materials

for

Recycling of Homogeneous Pd Catalysts Using Superparamagnetic Nanoparticles as Novel Supports for Suzuki, Heck, and Sonogashira Cross-Coupling Reactions

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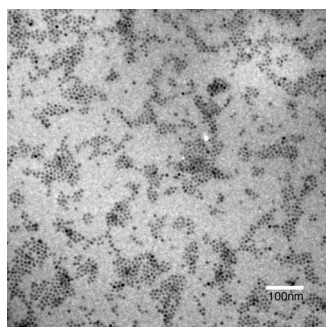
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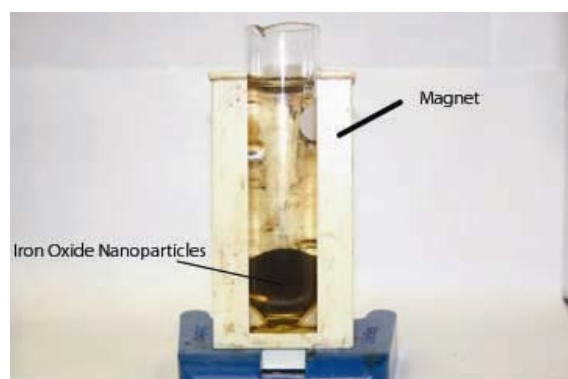
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Materials and Instrumentation. Chemicals were purchased from Acros Organics (Somerville, NJ), and Aldrich (Milwaukee, WI) and used as received without further purification. Water was obtained from a Milli-Q reagent water system purchased from Millipore Corporation (Milford, MA). ^1H NMR and ^{13}C data were obtained on a Varian VXR-300 system with an Oxford wide-bore magnet and the chemical shifts were reported in parts per million (ppm) downfield relative to tetramethylsilane using the residual proton resonance of solvents as the references (^1H NMR): CDCl_3 δ 7.27; CD_2Cl_2 δ 5.32 and (^{13}C NMR): CDCl_3 δ 77.2; CD_2Cl_2 δ 54.0. TEM measurements were accomplished with a Hitachi H7100FA operating at an accelerating voltage of 75 or 100kV. Iron oxide nanoparticle specimens were deposited onto Formvar- and silicon-coated, 200 mesh copper grids (Structure Probe, Inc., West Chester, PA) and the edge of the grid touched to a filter paper to wick away most of the solvent. Images were recorded either on conventional photographic films or captured using a Gatan 789 digital camera. Magnification was calibrated using a MAG*I*CAL high resolution magnification standard accurate to $1 \times 10^6 \times$. The permanent magnet (LifeSepTM 50sx magnetic separator) was purchased from Dexter Magnetic Technologies (Elk Grove Village, IL). Gas chromatography (GC) analyses were performed on a Varian 3900 GC system installed with a thermo-conductive detector and a Zebron ZB-5 capillary GC column with a 0.25 mm ID. Anisole was employed as an internal standard in our GC analyses unless an alternative was mentioned. A typical GC analysis program used a temperature gradient with an initial column temperature of 50 °C, which was gradually increased to a final temperature of 320 °C in 15 min. Elemental analyses were done in Galbraith Laboratories, Inc. (Knoxville, TN).



TEM micrograph of our maghemite nanoparticles.



Magnetic concentration of maghemite nanoparticles using a permanent magnet (LifeSepTM 50sx magnetic separator). Nanoparticles are concentrated on the side wall of a 50-mL centrifugation tube.

Synthesis of the Iron Oxide Nanoparticle Supported-Pd Catalyst (Iron Oxide-Pd).

About 60 mg of 11-nm γ -Fe₂O₃ nanocrystals coated with oleate¹ in 50 mL of chloroform was treated with (3-chloropropyl)trimethoxysilane (1 mL, 5.48 mmol). The resulting solution was then brought to reflux. After 12 h, the solution was cooled down to ambient temperature. Nanoparticles were magnetically concentrated by using an external permanent magnet (LifeSepTM 50sx magnetic separator) and washed with toluene (2 x 50 mL), 0.1 M HCl (2 x 50 mL) and methanol (2 x 50 mL). The resulting nanoclusters were air-dried. Such nanoparticles were re-dissolved in 45 mL of dry toluene and then *N*-methylimidazole (0.75 mL, 9.41 mmol) in 5 mL of toluene was added. The resulting solution was brought to reflux and after 16 h, it was cooled down to room temperature. Nanoparticles were then magnetically concentrated and washed with toluene, HCl and methanol sequentially.

About 100 mg of the aforementioned magnetic nanoparticles were re-dissolved in a mixture of DMF (2 mL) and Na₂CO₃ aqueous solution (0.5 M, 2 mL) in the presence of Pd(OAc)₂ (22 mg, 98 μ mol). After 16 h at 50°C, the mixture was cooled down to room temperature. The nanoparticle-Pd composites were magnetically concentrated and washed with water (3 x 50 mL), 0.1 M HCl (3 x 50 mL), methanol (3 x 50 mL) and air-dried. The amount of Pd on the nanoparticles was determined elemental analysis.

Preparation of the Polystyrene Resin-Supported Pd Catalyst (Solid Phase-Pd).

A mixture of chloromethyl polystyrene (CM PS) (2% DVB crosslinking, 3.0g) and *N*-methylimidazole (3mL, 36.9 mmol) in *N*-methyl-2-pyrrolidinone (NMP) (300 mL) was stirred at 80°C for 16h. After cooling down, the solids were separated from reaction mixtures via filtration and washed with NMP (5 x 20 mL), 0.1 M HCl aqueous solution (5 x 20 mL) and methanol (5 x 20mL) sequentially. The solid residues were then dried under reduced pressure to yield brownish resins (2.27g).

To the resulting imidazolium-polystyrene resins (1 g) suspended in 10 mL of DMF was added Pd(OAc)₂ (90 mg, 0.4 mmol) and an aqueous solution (8 mL) of Na₂CO₃ (424 mg, 4.0 mmol). The mixtures were sonicated at room temperature for 30 min and then stirred at 50°C for 3 h. Solid resins were separated via filtration and washed with distilled water (6 x 20 mL) and methanol (6 x 20 mL) sequentially. The solid residues were then dried under reduced pressure to yield black powders of **Solid Phase-Pd**. The amount of Pd on the resins was determined by elemental analysis.

General Procedure for Suzuki Cross-Coupling Reactions

A 50 mL flask fitted with a reflux condenser and septum was charged with an aryl halide (0.5 mmol), phenyl boronic acid (0.55 mmol, 67 mg) and potassium carbonate (138 mg). The palladium catalyst (**Solid Phase-Pd**: 138 mg or **Iron Oxide-Pd**: 25 mg) (7.3 mol%) in DMF (10 mL) was injected. The mixture was stirred at 50°C. To monitor the reaction, a 500 μ L of the reaction solution was taken out at a fixed interval. For the reaction catalyzed by **Solid Phase-Pd**, samples were filtered through a 0.2 μ m Anotop syringe filter (Whatman, Florham Park, NJ) before a GC injection. For the reaction under **Solution-Pd**, samples were washed with 1 mL of dilute hydrochloric acid (5%) and extracted with 500 μ L of toluene. The organic phase was dried and used for GC analyses. For the reaction under **Iron Oxide-Pd**, a magnet was used to remove the nanoparticles, and the solutions were filtered through a 0.2 μ m filter before GC analyses. Anisole was used as an internal standard for our GC experiments.

General Procedure for Heck Cross-Coupling Reactions

A 50 mL flask fitted with a reflux condenser and septum was charged with an aryl halide (0.5 mmol), and sodium carbonate (2.5 mmol, 265 mg). The palladium catalyst (**Solid Phase-Pd**: 138 mg or **Iron Oxide-Pd**: 25 mg) (7.3 mol%) and *n*-butyl acrylate (0.55 mmol, 76.9 mg) in a mixture of water (2 mL) and DMF (10 mL) were added. The mixture was stirred at 50 °C. GC analyses were followed using the procedure similar to the one in Suzuki reactions.

General Procedure for Sonogashira Cross-Coupling Reactions

A 50 mL flask fitted with a reflux condenser and septum was charged with an aryl halide (0.5 mmol) and sodium carbonate (2.5 mmol). The palladium catalyst (**Solid Phase-Pd**: 138 mg or **Iron Oxide-Pd**: 25 mg) (7.3 mol%) and phenylacetylene (0.55 mmol, 61.2 mg) and copper(I) iodide (0.08 mmol, 15 mg) in a mixture of water (2 mL) and DMF (10 mL) were added. The mixture was stirred at 50 °C. The reaction progress was monitored by GC analyses.

Reference:

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