Electronic Supplementary Information (ESI)

Polysilane-Supported Pd and Pt Nanoparticles as Efficient Catalysts for Organic Synthesis

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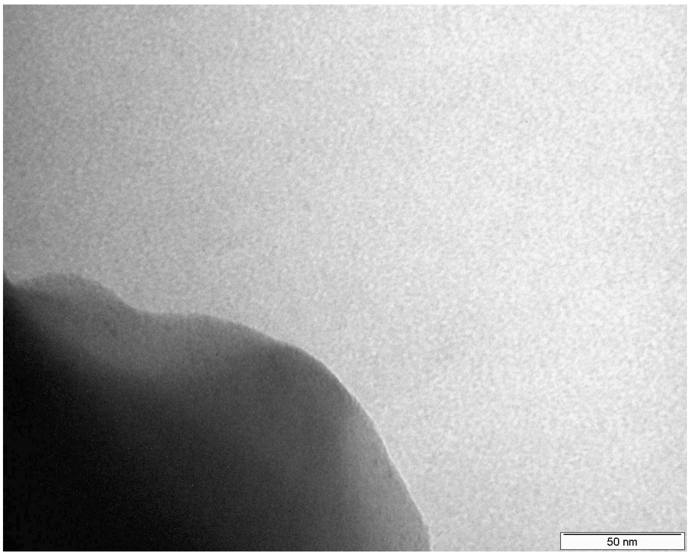
Synthesis of poly(methylphenylsilane) (**1**): Methylphenyldichlorosilane (382 g, 2.00 mol) was added dropwise to a suspension of sodium (96.6 g, 4.20 mol) in THF (1 L) for 30 min with vigourous stirring at reflux temperature. After stirring for further 3.5 h, the mixture was cooled in an ice bath and diluted with toluene (500 mL). 3N HCl (500 mL) was dropwise to the mixture, the organic layer was separated and water was added to the aqueous layer to dissolve NaCl. The aqueous layer was extracted with toluene and the combined organic layers were washed with H_2O, 5% aqueous solution of $NaHCO_3$, H_2O and brine. The organic layer was dried over Na_2SO_4 and concentrated to ca. 600 mL in *vacuo*. MeOH (750 mL) was added to the solution, the precipitate was collected by filtration and washed with MeOH. The crude polysilane was dissolved in toluene (370 mL) and precipitated by adding *i*PrOH. The precipitate was collected, washed with toluene–*i*PrOH (1/5) and dried under reduced pressure at 55 °C to afford poly(methylphenylsilane) (**1**, 135 g, 56% yield). Mw = 3.21 x 10 ^{4} , Mn = 1.12 x 10 ^{4}, Mw/Mn = 2.87.

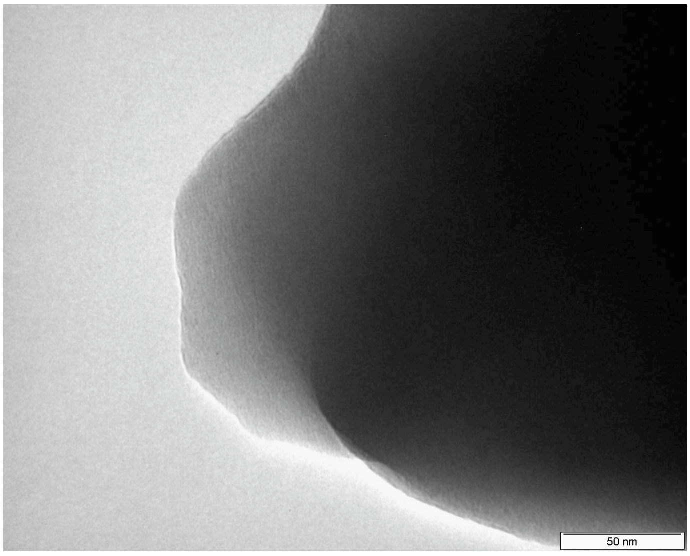
Preparation of PSi-Pd 2b: Poly(methylphenylsilane) (**1**, 10.0 g) was dissolved in THF (80 mL) and cooled to 0 °C. To this solution, palladium (II) acetate (225 mg, 1.00 mmol) was added. The mixture was stirred for 1 h at this temperature and allowed to warm to rt. After 2 h, MeOH (400 mL) was slowly added for coacervation and the resulting precipitate was collected by filtration, washed with MeOH several times and dried under reduced pressure at 55 °C. The polysilane-supported palladium catalyst (PSi-Pd **2b**, 7.17 g, Pd = 0.134 mmol/g, 96% of Pd was loaded) was obtained. Loading of Pd was determined by ICP analysis after decomposition of the catalyst with sulfuric acid and nitric acid at 180 °C.

SEM images of **2a, 2b,** and **2f** were shown below. While **2f** showed formation of larger clusters, no clusters were observed in **2a** and **2b** in these images. This suggested that smaller clusters (< 1nm) were formed in **2a** and **2b**.

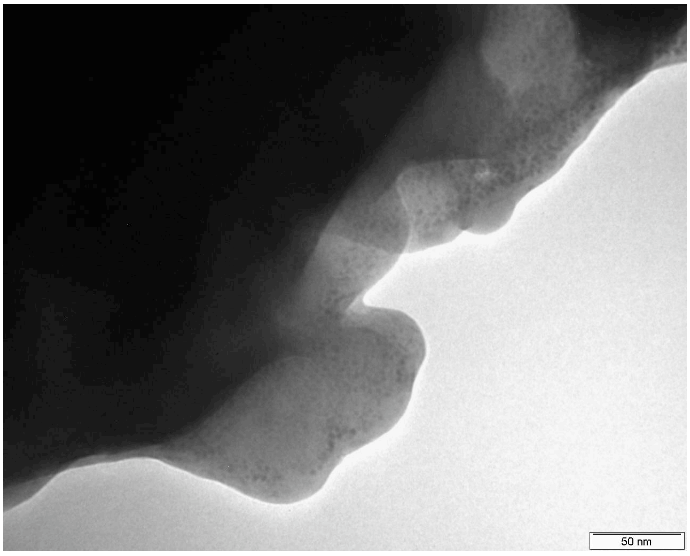
2a:



2b:



2f:



Typical experimental procedure for hydrogenation: PSi-Pd **2b** (0.5 mol%) and a substrate (1.00 mmol) were combined in hexane (3 mL) at rt. The mixture was stirred for the time indicared in Table 2 at rt with hydrogen bubbling. The catalyst was then filtered and washed with hexane, and the solvent of the filtrate was removed in *vacuo*. The yields of the products were estimated by ^{1}H NMR analysis using 1,2,4,5-tetramethylbenzene (durene) as an internal standard. Leaching of Pd was determined by ICP analysis.

Suzuki reaction: PSi-Pd **2b** (0.0125 mmol), bromoacetophenone (50 mg, 0.25 mmol), phenylboronic acid (45.7 mg, 0.375 mmol), $P(o\text{-}MeOC_6H_4)_3$ (4.4 mg, 0.0125 mmol), and potassium carbonate (69.1 mg, 0.5 mmol) were combined in EtOH (2.5 mL) under argon atmosphere. The mixture was stirred at 80 °C for 2 h and cooled. After hexane was added to quench the reaction, the catalyst was collected by filtration. The sample solution was evaporated and the residual of the crude product was purified by preparative thin-layer chromatography (PTLC) to afford 4-acetylbiphenyl (45.9 mg, 94%).

Sonogashira reaction: PSi-Pd **2b** (0.0125 mmol), iodobenzene (28 μL, 0.25 mmol), phenylacetylene (35.7 μL, 0.325 mmol), and potassium carbonate (69.1 mg, 0.5 mmol) were combined in EtOH (2.5 mL) under argon atmosphere. The mixture was stirred at 80 ºC for 12 h and cooled. After hexane was added to quench the reaction, the catalyst was collected by filtration. The solvents of the filtrate were then removed under reduced pressure. The yield of diphenylacetylene was determined by GC analysis using naphthalene as an internal standard.

Preparation of PSi-Pt 3: Poly(methylphenylsilane) (**1**, 10.0 g) and hydrogen hexachlororplatinate (IV) hexahydrate (518 mg, 1.00 mmol) were dissolved in THF (80 mL) at rt, and triethoxysilane (1.84 mL, 10.0 mmol) was added to this solution. The mixture was stirred for 24 h, and MeOH (400 mL) was slowly added for coacervation. The resulting precipitate was collected by filtration, washed with MeOH several times and dried under reduced pressure at 55 ºC. The polysilane-supported platinum catalyst (PSi-Pt **3**, 8.98 g, Pt = 0.0725 mmol/g, 65% of Pt was loaded) was obtained. The loading of Pt was determined by ICP analysis after decomposition of the catalyst with hydrofluoric acid, nitric acid and aqua regia at 180 ºC.

Hydrosilylation using PSi-Pt 3: PSi-Pt **3** (200 mg, 14.5 mmol, 3.6 mol %) and 4,4-diphenyl-1-butene (**4**, 83.3 mg, 0.40 mmol) were combined in hexane (2 mL), and triethoxysilane (110 mL, 0.60 mmol) was added to this mixture. The mixture was stirred for 2 h at rt. The catalyst was filtered and washed with hexane, and the solvent of filtrate was removed in *vacuo*. The yields of the products were estimated by ^{1}H NMR analysis using 1,2,4,5-tetramethylbenzene (durene) as an internal standard. The leaching of Pt was determined by ICP analysis after decomposition of the filtrate with hydrofluoric acid, nitric acid and aqua regia at 180 °C. Recovered PSi-Pt **3** was dried under reduced pressure.