

Supplementary Information

Synthesis of a recyclable and efficient Pd(II) 4-(2-pyridyl)-1, 2, 3-Triazole Complex over the solid Periodic Mesoporous Organosilica support by “Click reactions” for the Stille coupling reaction

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Experimental Section

Hybrid mesoporous materials were synthesized using C16 hexadecyltrimethyl ammonium bromide as surfactant and 1, 2-bis (triethoxysilyl) benzene (BTEB) and tetraethyl orthosilicate (TEOS) as the silica sources. 3-chloropropyl trimethoxysilane (3-CIPTMS), 2-ethynylpyridine, copper iodide, sodium azide, olefins and aryl halide purchased from Aldrich. All solvents used in these experiments were obtained from Merck (India) and dried before use according to standard methods. All chemicals were purchased from Aldrich Chemicals and used as received.

Powder X-ray diffractograms (XRD) of the materials were recorded using a PANalytical X'pert Pro dual goniometer diffractometer. The radiation used was Cu K α (1.5418 Å) with a Ni filter and the data collection was carried out using a flat holder in Bragg-Brentano geometry (0.5 to 5°; 0.2°/min). N₂ adsorption–desorption isotherms, pore size distributions as well as the textural properties of the hybrid materials were determined by using a Micromeritics ASAP 2020 instrument and Autosorb 1C Quantachrome USA. Pore size distribution curves were obtained via the NLDFT model assuming cylindrical pore geometry (BJH desorption pore size distribution) and the micropore volume calculated via t-plot analyses as a function of relative pressure using the Broekhoff de Boer model for thickness curve measured between 3.5-5.0 Å. A JEOL JEM-3010 and Tecnai (Model F30) both operating at 300KV were used for HRTEM samples observation. Chemical analysis was carried out in a Lab Tam 8440 Plasma lab sequential mode ICP-OES Spectrometer and a Spectro Arcos ICP-OES instrument. The scanning electron micrographs of the samples were obtained in dual beam scanning electron microscope (FEI company, model Quanta 200 3D) operating at 30 kV. The samples were loaded on stubs and sputtered with thin gold film to prevent surface charging and also to protect from thermal damage due to electron beam. ¹H NMR spectra were recorded on Bruker AC-200 instruments using deuteriated solvent. Chemical shifts are reported in ppm. Liquid ¹³C NMR spectra were recorded on Bruker AC-200 instruments operating at 50 MHz. ¹³C NMR chemical shifts are reported in ppm relative to the central line of CDCl₃ (d 77.0). Solid-state ¹³C CP MAS NMR and ²⁹Si MAS NMR spectra were recorded on a Bruker MSL 300 NMR spectrometer with a resonance frequency of 75.5 MHz and 59.6 MHz for ¹³C and ²⁹Si, and the chemical shifts were referenced to glycine and TMS respectively. Infrared spectra were recorded using a Perkin Elmer, Spectrum one FTIR spectrophotometer. The liquid samples or dilute solution of the solid samples in THF were spread over KBr plates, and their spectra were recorded. Thermal analysis (TG-DTA) of the samples was conducted using a Pyris Diamond TGA analyzer with a heating rate of 10°C min⁻¹ under air atmosphere. XPS of Palladium core levels was studied using an ambient pressure photoelectron spectrometer and more details of the instrument are available in reference 1.

Azide functionalization over benzene PMO (B-PMO-N₃): Surface modification of benzene containing periodic organosilica material (B-PMO) with 3-azidopropyltrimethoxysilane (Az-PTMS) was achieved by a post grafting method. To a suspension of 1 g of B-PMO in 50 ml of toluene, 2 ml 3-azidopropyl trimethoxysilane (Az-PTMS) was added, and the mixture was stirred for 18 h at 90°C under nitrogen atmosphere. After the completion of reaction, the contents were cooled, filtered and washed with toluene to remove extra unreacted 3-Az-PTMS. The sample was then dried at 80°C for 8 h in a vacuum oven and preserved under argon atmosphere for further use [Scheme.1.(B)]. The obtained material is abbreviated as B-PMO-N₃. Yield: 1.15 g (solid). ¹³C NMR: 11.49, 24, 55, 135.

Click chemistry between 2-ethynylpyridine and B-PMO-N₃ : In a 20 ml capped vial with a magnetic stir bar, copper iodide (1 mg) and vacuum distilled N,N-diisopropylethylamine (DIPEA) (2 mg) were charged with anhydrous, nitrogen-purged dimethylformamide (DMF) (2.5 ml). The mixture was stirred until the solution turned green and transferred to an anhydrous, nitrogen-purged tetrahydrofuran (THF) reaction mixture (7.5 ml) containing 3-azidopropyltrimethoxysilane mesoporous organosilica material (PMO-N₃) (500 mg). The reaction mixture was stirred for additional 20 min before the 2-ethynylpyridine (10 mmol) were added and stirred at 50°C for 24 h. After cooling down to room temperature, the obtained sample was ultrasonicated for 10 min, rinsed with THF, and dried with nitrogen. The sample was kept in desiccators in the absence of light for further characterization and modification [Scheme.1.(C)]. The obtained material is designated as B-PMO-TZ. ¹³C NMR: 11, 24, 55, 124, 135, 149, 156.

Metalation over the B-PMO-TZ surface by PdCl₂ : A solution of PdCl₂ (0.216 g, 1.22 mmol) in DMSO (50 ml) was added to the (2.01 g) of 4-(2-pyridyl)-1, 2, 3 triazole ligand benzene PMO material (B-PMO-TZ). The reaction mixture was refluxed under argon for 24 h. The product was allowed to cool and filtered. The yellow solid was washed with DMSO (30 ml) and acetone (30 ml). Further, product was Soxhlet-extracted with dichloromethane (CH₂Cl₂) for 24 h to remove physically adsorbed PdCl₂ and organic moieties. The resulting product was dried under vacuum at 60°C to give 1.93 g of the grey colour B-PMO-TZ-Pd(II) [Scheme.1.(D)].

Reference

- [1] K. Roy, C. P. Vinod and C. S. Gopinath, J. Phys. Chem. C, 2013, 117, 4717-4726.

¹H NMR (CDCl₃) and ¹³C NMR of coupled products

(a) biphenyl

¹H NMR (CDCl₃): 7.34-7.62 (m, 10H).

¹³C NMR (CDCl₃): 127.20 (s, 5C), 128.79 (s, 5C).

(b) 4-nitro-1,1'-biphenyl

¹H NMR (CDCl₃): 7.40-7.44 (m, 3H), 7.54-7.59(m, 2H), 7.65-7.69 (m, 2H), 8.21-8.26 (d, 2H).

¹³C NMR (CDCl₃): 123.09 (s, 2C), 126.37 (s, 2C), 126.78 (s, 2C), 127.89 (s, 1C) 128.13 (s, 2C), 137.77 (s, 2C), 146.62 (s, 2C).

(c) 4-methyl-1, 1'-biphenyl

¹H NMR (CDCl₃): 2.32 (s, 3H), 7.16-7.53 (m, 9H).

¹³C NMR (CDCl₃): 21.14 (s, 1C), 127.02 (s, 5C), 128.75 (s, 2C), 129.52 (s, 2C), 137.06 (s, 1C) 138.39 (s, 1C), 141.19 (s, 1C).

(d) 4-methoxy-1, 1'-biphenyl

¹H NMR (CDCl₃): 3.83 (s, 3H), 6.96-6.99 (d, 2H), 7.29-7.32 (m, 1H), 7.37-7.41 (m, 2H), 7.50-7.57 (m, 4H).

¹³C NMR (CDCl₃): 55.38 (s, 1C), 114.26 (s, 2C), 126.71(s, 1C) 126.78 (s, 2C), 128.20 (s, 2C), 128.77 (s, 2C), 133.83 (s, 1C), 140.88 (s, 1C), 159.21(s, 1C).

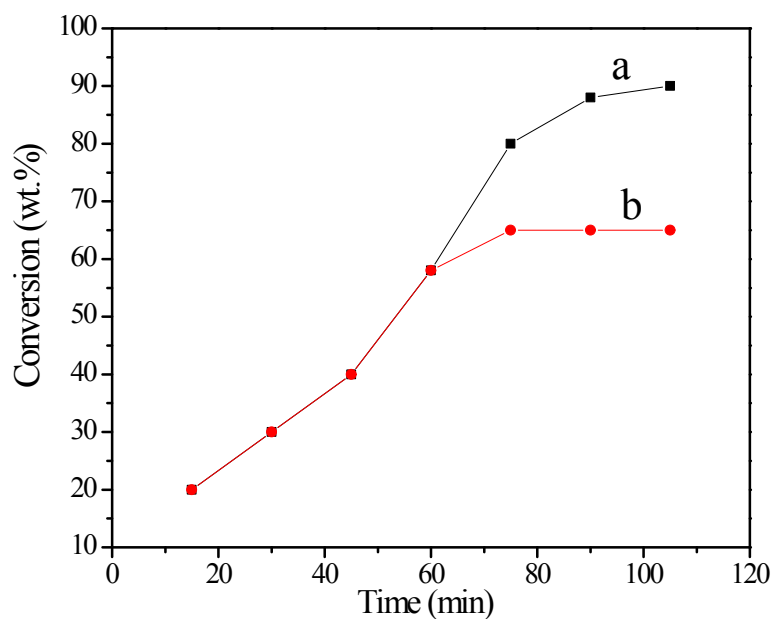


Fig.S1. Leaching studies (hot filtration test) performed With (a) complete run, (b) filtrate removed after 60 min; reaction conditions: : iodobenzene (1mmol), phenyltributyltin (1.15 mmol), base Cesium fluoride (CsF) (3 mmol), DMSO solvent (3 mL), with heterogeneous B-PMO-TZ-Pd(II) catalyst (30 mg), Temperature 120 °C.