



Anchoring of palladium(II) in chemically modified mesoporous silica: An efficient heterogeneous catalyst for Suzuki cross-coupling reaction

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ABSTRACT

The synthesis and characterization of a highly efficient and reusable catalyst, Pd(II) immobilized in mesoporous silica MCM-41, are described. Pd(II) Schiff-base moiety has been anchored onto mesoporous silica surface via silicon alkoxide chemistry. The catalyst has been characterized by small-angle X-ray diffraction (SAX), FTIR and electronic spectroscopy as well as elemental analysis. The catalyst is used in Suzuki cross-coupling reaction of various aryl halides, including less reactive chlorobenzene, and phenylboronic acid to give biaryls in excellent yields without any additive or ligand. High selectivity for the biaryl products containing both electron-donating and electron-withdrawing substituents, mild reaction conditions and possibility of easy recycle makes the catalyst highly desirable to address the industrial needs and environmental concerns.

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1. Introduction

Suzuki coupling is an important reaction in organic chemistry for the selective synthesis of biaryls [1]. Biaryls have widespread applications in the synthesis of natural products, pharmaceuticals, and advanced materials [2–5]. The utility of the Suzuki reaction comes from its relative thermal stability, insensitivity to air or moisture, broad functional group tolerance, as well as low toxicity associated with boron compounds. Many palladium complexes have been used as homogeneous catalysts for Suzuki reaction [6–8]. Although homogeneous catalytic systems are known to exhibit better activity than heterogeneous systems but for the large scale applications in liquid phase reactions, it causes greater difficulties such as purification of the final product, recycling of the catalyst, and deactivation via aggregation into inactive Pd particles. Further removal of Pd from organic products at the end of the reaction is highly desirable because of its high cost and toxicity. So the development of heterogeneous systems where the metal is grafted on inorganic or organic supports has attracted much attention in recent years [9–11]. The mesoporous silica-based materials designated as M41S have attracted a lot of attention in catalysis study [12] since its invention by the scientists of Mobil Corporation [13,14]. MCM-41 is one of the members of this family having uniform hexagonal arrays of one-dimensional channels of mesop-

ores with a pore diameter in the range of 20–100 Å. As regards the preparation and characterization of porous silica-based heterogeneous catalyst for cross-coupling reactions few studies deserve particular mention. It is reported that catalysts derived from anchoring of Pd(II) complex into MCM-41 showed high catalytic activity and recyclability for the Mizoroki–Heck reaction [15,16]. High activity and selectivity in the carbon–carbon coupling reaction is also obtained using catalyst prepared by immobilization of Pd on silica modified with methyl or phenyl groups [17]. Pd nanoparticles dispersed on amine-functionalized zeolites and mesoporous silica are found to be highly active in Heck reactions [18,19]. Recently, we have developed Pd(0) immobilized mesoporous silica catalyst which efficiently catalyzes various C–C coupling reactions like Heck, Sonogashira, Suzuki, Stille reactions [20,21]. Palladium complexes have been immobilized on mercaptopropyl-functionalized SBA-16 and KIT-6 to catalyze Suzuki–Miyaura reaction [22].

Wiedermann reported a series of square-planar *trans*-dichloro palladium(II) complexes containing *N*-(2-thienylmethylene)-aniline and *N*-(2-thienylmethyl)-aniline ligands that exhibit high catalytic activity in the Suzuki cross-coupling reaction [23]. Inspired by this ligand system, we have synthesized heterogeneous catalyst using similar type of ligand system.

Herein, we describe preparation, characterization and catalytic efficacy of a new heterogeneous palladium based catalyst for Suzuki cross-coupling reaction. The catalyst is active towards various aryl halides including less active chlorobenzene as well as *para*-chloroacetophenone under mild reaction conditions.

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2. Experimental

2.1. Materials

PdCl₂ (>99.9%), tetraethyl orthosilicate (TEOS, 98%), the cationic surfactant cetyltrimethylammonium bromide (CTAB, 98%), 3-mercaptopropyl-functionalized silica (SH-SiO₂) [sulfur content of SH-SiO₂ = 3.95 wt%], and all other reagents were purchased either from Sigma-Aldrich/Fluka or Alfa-Aesar and were used as received without further purification. The solvents were purchased from Merck (India) and were distilled and dried before use.

2.2. Synthesis of siliceous MCM-41

MCM-41 was synthesized according to the literature method [24] by the hydrolysis of the structure directing agent CTAB (cetyltrimethylammonium bromide) and tetraethyl orthosilicate (TEOS), in basic solution with a molar composition of the reactants 1.0 CTAB:7.5 TEOS:1.8 NaOH:500 H₂O. The gelatinous mixture was then hydrothermally treated at 110 °C for 60 h in a Teflon lined autoclave. After cooling to room temperature the resultant solid was recovered by filtration, washed with deionized water and dried in air. The collected product was calcined at 823 K for 8 h to remove the occluded polymeric surfactants.

2.3. Organic modification of MCM-41 with (3-aminopropyl)-triethoxysilane (3-APTES)

Post synthesis organic modification of the mesoporous material was performed by stirring 0.3 g of MCM-41 with 0.004 mmol of 3-APTES in dry chloroform (20 ml) at room temperature for 12 h under nitrogen atmosphere. The resulting white solid MCM-41-(SiCH₂CH₂CH₂NH₂)_x was filtered, and washed with chloroform followed by dichloromethane and dried in air.

2.4. Schiff base generation in APTES modified MCM-41 using 2-thiophenecarboxaldehyde

The white solid, MCM-41-(SiCH₂CH₂CH₂NH₂)_x was refluxed with 50 mg (0.45 mmol) of 2-thiophenecarboxaldehyde in methanol at 60 °C for 8 h. The resulting cream colored solid was filtered, washed with methanol followed by dichloromethane and dried in air.

2.5. Anchoring of Pd(II) in modified MCM-41

Pd(II)-MCM-41 was prepared by refluxing Schiff base containing cream colored solid with 5 mg of PdCl₂ in 20 ml acetone for 72 h. The light yellow solid thus formed was then filtered, dried and washed with acetone using Soxhlet for 12 h to remove any unanchored palladium species and dried under vacuum. The Pd content of the catalyst found to be 0.3 (wt%) (2.82 × 10⁻³ mol%). Elemental analysis showed Pd:C and Pd:N were 15.62 and 1.84, respectively.

2.6. Catalyst characterization

The powder X-ray diffraction (XRD) patterns of the samples were recorded on a Scintag XDS-2000 diffractometer using Cu K α radiation. Fourier transform infrared (FTIR) spectra of KBr pellets were measured on a Perkin Elmer RX1 FTIR spectrometer. Electronic spectra were measured on a Shimadzu CP-3101 UV-Vis spectrophotometer. The palladium content of the sample was determined by Perkin Elmer A-Analyst 200 atomic absorption spectrometer. Elemental analysis, for carbon, hydrogen, and

nitrogen (CHN), was undertaken on a Perkin Elmer 240C elemental analyzer. Other instruments used in this study were the same as reported earlier [25,26]. ¹H NMR spectra were measured on a Bruker Avance DPX 300 NMR (300 MHz) spectrometer using TMS as the internal standard. To study the progress of the reaction the products were collected at different time intervals and identified and quantified by a Varian CP-3800 Gas chromatograph using a CP-Sil 8 CB capillary column.

2.7. General experimental procedure for Suzuki cross-coupling reaction

The coupling reaction was carried out in a glass batch reactor. At first aryl halide (3 mmol) and phenylboronic acid (0.4 g, 3.3 mmol) were dissolved in 4 ml ethanol. This reactant mixture was then added to the solution of Na₂CO₃ (0.318 g, 3 mmol) in 1 ml of water under stirring condition. To this 0.01 g of Pd(II)-MCM-41 catalyst was added and the reaction mixture was heated to 60 °C in an oil bath. For isolation of products at the end of the catalytic reaction, the catalyst was first separated out by filtration and then the filtrate was extracted four times with diethyl ether (4 × 10 ml). The organic layers thus collected were combined and washed with water to remove excess Na₂CO₃ and finally washed with brine and dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by column chromatography over silica gel (mesh 60–120) using *n*-hexane/ethyl acetate mixture as eluent to give the desired product. The product was analyzed by GC and ¹H NMR. All of the products were well-known and reported in the literature. The spectroscopic data (¹H NMR) of these products are consistent with those previously reported values.

2.8. Heterogeneity tests

2.8.1. Hot filtration test

A mixture of iodobenzene (3 mmol), phenylboronic acid (0.4 g, 3.3 mmol), Na₂CO₃ (0.318 g, 3 mmol), Pd(II)-MCM-41 (2.82 × 10⁻³ mol%) in 5 ml of 20% H₂O/EtOH was stirred at 60 °C and the progress of the reaction was monitored by GC analysis. After 30% completion of the reaction (analyzed by GC), the catalyst was separated at the reaction temperature (to avoid re-deposition of leached Pd species on the catalyst surface during cooling of the reaction mixture) by centrifugation and the reaction solution was stirred at that temperature for another 2 h. There was no further increase in the product concentration, as determined by GC analysis.

2.8.2. Solid-phase poisoning test

A mixture of SH-SiO₂ (0.10 g, 0.12 mmol) and 0.01 g of Pd(II)-MCM-41 catalyst were taken in the solution containing arylhalides (3 mmol), phenylboronic acid (0.4 g, 3.3 mmol) and Na₂CO₃ (0.318 g, 3 mmol) in 5 ml of 20% H₂O/EtOH. The mixture was stirred continuously maintaining the temperature of the oil bath at 60 °C. The progress of the reactions was monitored by the method described above.

3. Results and discussion

3.1. XRD studies

The small-angle X-ray diffraction patterns of MCM-41 and the catalyst Pd(II)-MCM-41 are shown in Fig. 1. The pristine MCM-41 shows a typical three-peak pattern [14,27] with a very intense *d*₁₀₀ = 38.85 Å diffraction peak at $2\theta \approx 2.27^\circ$ and two other weaker peaks at $2\theta \approx 3.99^\circ$ and $2\theta \approx 4.58^\circ$ for *d*₁₁₀ and *d*₂₀₀, respectively. MCM-41 shows an additional peak at $2\theta \approx 6.16^\circ$ which can be assigned to *d*₂₁₀ reflection. All the peaks are well-resolved

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