Journal of Molecular Catalysis A: Chemical 407 (2015) 87–92

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

# Palladium(II) supported on polycarbosilane: Application as reusable catalyst for Heck reaction

Kunniyur Mangala, P.S. Sinija, Krishnapillai Sreekumar*

*Department of Applied Chemistry, Cochin University of Science and Technology, Cochin 682022, Kerala, India*

ARTICLE INFO

*Article history:*
Received 4 December 2014
Received in revised form 23 May 2015
Accepted 11 June 2015
Available online 17 June 2015

*Keywords:*
Polycarbosilane
Heck reaction
Palladium catalyst
Heterogeneous catalysis

ABSTRACT

Heck reaction catalyzed by palladium(II) attached polycarbosilane is reported. Polycarbosilane (PCS), which is an organic-inorganic hybrid polymer containing both Si and C in its back bone structure, was synthesized by the polycondensation of trichloromethylsilane and trimethoxyvinylsilane in the presence of sodium metal. Palladium acetate was attached to the polycarbosilane (Pd-PCS) and its catalytic activity was investigated. Heck reaction in which C–C coupling between aryl halides or vinyl halides and activated alkenes in the presence of a base has been selected for the study. Palladium ions supported on PCS have been used as a catalyst for the first time and it efficiently catalyzed Heck reaction and an yield of 75–90% was obtained with different substrates. For comparison, catalytic activities of Pd ions supported on SBA-15, activated charcoal and amorphous silica were also investigated. Results indicate the superior activity of Pd-PCS.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

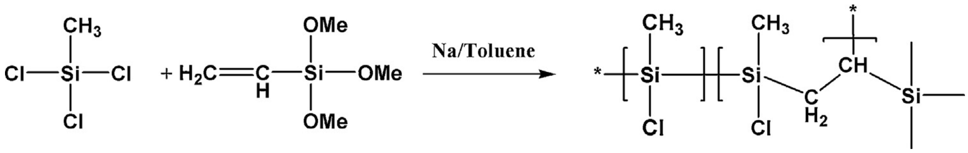
Polycarbosilane (PCS) has considerable technological importance due to its high thermal, chemical and oxidative stability. It is not hard to envision a variety of potential applications that are opening up for these polymers in areas such as nanotechnology [1], surface science, catalysis [2–6], liquid crystals [7–9], new ceramic materials [10–14], organic-inorganic hybrids etc. PCS, which contains both Si and C in their back bone structure, have been of particular importance as precursor to SiC [15–21]. PCS can be prepared in one step from simple silane monomers or mixtures containing vinyl, halo or halomethyl moieties in the presence of an active metal. Several investigators have explored the use of alkali metals for the reductive coupling of silanes and vinyl silanes [11–14,16,18–21]. The participation of vinyl groups produces partial branching. The Wurtz type coupling reaction, which employs alkali metals, can be used for the preparation of PCS. It generally leads to extensive crosslinking and appreciable Si—Si and C—C bonding in addition to SiC bonding [15–17]. A reasonable ceramic yield is obtained after sufficient crosslinking which increases the softening temperature and decreases the solubility. The highly crosslinked nature of the PCS provides scope for high surface area for the polymer [4,5]. High surface area is one of the main criteria for materials which are used as solid supports in heterogeneous catalysis.

Homogeneous catalytic processes often exhibit high activity and selectivity, in most cases, but the catalyst-product separation is generally nontrivial. In addition, the metal catalysts and ligands can be very expensive. These limit the practical application of many outstanding catalytic systems. Immobilization of analogues of homogeneous catalysts on a solid support is one of the promising ways to prepare well-defined catalytic systems, a task of great economic and environmental importance [22–24]. Palladium catalysts deposited over different types of solid supports such as silica matrices, charcoal etc have been reported [25–28]. However, activated charcoal and non-functionalized polymers have drawbacks such as relatively low stability or lack of active functional groups for binding Pd ions and hence the inherent restrictions for reuse [28]. Since C and $SiO_2$ have only a small residual charge, their affinity for metal ions will be weak. Silica is a favorable solid support, but if silica is used directly, the main problem of these catalytic systems seems to be the metal leaching from the support during the reaction even though they adsorb back to the support after the completion of the reaction [27]. Polymer supported transition metal ions have significant role as catalysts in various organic reactions [4,5,29,30]. The metal ions are attached to the polymer support through a chemical bond. This reduces the possibility of leaching of metal ions from the solid support. Considering Pd ions as a homogeneous catalyst, they easily lose catalytic activity by forming Pd clusters and also they are highly expensive. A heterogeneous catalyst is desirable in this

---

* Corresponding author. Fax: +91 484 2577595.
*E-mail address:* ksk@cusat.ac.in (K. Sreekumar).

http://dx.doi.org/10.1016/j.molcata.2015.06.012
1381-1169/© 2015 Elsevier B.V. All rights reserved.



**Scheme 1.** Synthesis of polycarbosilane.

case, especially for recycling, though it is not always as reactive as compared to homogeneous catalysts.

Palladium catalysis has achieved the status of an indispensable tool for both common and state-of-the art organic synthesis. Among basic types of palladium catalysed transformations, the Heck reaction and related chemistry occupies a special space. Heck reaction is the catalytic arylation and alkenylation of olefins [31–35]. The reaction presents one of the simplest ways to obtain variously substituted olefins, dienes, and other unsaturated compounds. Aryl, benzyl, and styryl halides react with olefinic compounds in the presence of hindered amines and a catalytic amount of palladium ions to form vinyl derivatives in which the aryl, benzyl, or styryl group has replaced a vinyl hydrogen of the original olefin. To satisfy both recyclability and reactivity, immobilization of a reactive homogeneous catalyst was devised by binding the Pd catalyst on a polymer. Polycarbosilane is an active support for the heterogeneous catalysis. The PCS shows high thermal stability and have crosslinked structure. By altering the monomers and reaction time, it is possible to get sufficient crosslinking and active sites in the polymer. The metal salts react with the active sites of the PCS and stable bonds are formed between them, thus developing an efficient heterogeneous catalyst. $Pd(OAc)_2$ was chosen as Pd source for the current study. For comparison, catalytic activities of Pd ions supported on SBA-15 (Pd-SBA), activated charcoal (Pd-C) and amorphous silica (Pd-$SiO_2$) were also investigated. Pd-PCS show high stability, negligible metal leaching and can be reused with same activity. This indicates the superiority of PCS with other supports under consideration.

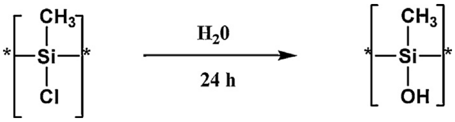
## 2. Experimental

### 2.1. Materials

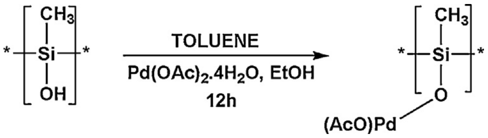
Monomers, trichloromethylsilane and trimethoxyvinylsilane, palladium acetate, SBA-15 and palladium(II) attached charcoal were purchased from Sigma–Aldrich, USA. DMF, triethyl amine, sodium, amorphous silica and sodium sulphate were purchased from Loba Chemie Pvt. Ltd., India. Chloroform, dichloromethane, diethyl ether, ethanol, methanol, toluene and all the substrates for catalytic activity studies were purchased from Spectrochem Pvt., Ltd., India; and all the solvents were purified according to standard procedures [36].

### 2.2. Characterization

FT-IR spectra were recorded on JASCO model 4100 FT-IR spectrometer as KBr pellets. $^{29}$Si-CP-MAS NMR and $^{13}$C CP-MAS-NMR spectra were obtained from NMR Research Center, IISc., Bangalore and National Chemical Laboratory, Pune. Thermogravimetric analysis was done on PerkinElmer Diamond model Pyris 6 TG/DTA system using Platinum as standard. Samples were heated under nitrogen atmosphere from 50 °C-1000 °C at a rate of 20 °C/min. The X- Ray Diffraction analysis was carried out using Rigaku (D-MAX Cu-Kα) X-ray Photometer. The sample was scanned over the range of 20–90° angles with an increment of 0.05° angle and with the rotation speed of 5°/min. (SAIF-CUSAT). Surface Area & porosity were measured using Micromeritics TriStar 3000 V6.07 A Surface area analyzer. The metal ion concentration was estimated using Thermo Electron Corporation Atomic Absorption Spectrometer. $^1$H NMR spectra were recorded on Bruker 400 MHz instrument with TMS as the internal standard in $CDCl_3$ (SAIF-CUSAT). In catalytic activity study, all the reactions were analyzed, by HPLC on Shimadzu CLASS VP Ver 6.1. Column: Phenomenex Luna 5u C18 (2) 100 Å, for yield and purity of the products. Solvent ratio ($CH_3OH$:$H_2O$) was 75:25 with a run time of 30 min. The flow rate, detector wavelength and the temperature were 1 mL/min, 254 nm and 28 °C, respectively.



**Scheme 2.** Conversion of chloride groups of PCS to hydroxyl groups.



**Scheme 3.** Incorporation of palladium ion to PCS.

### 2.3. Synthesis of PCS

In a 250-mL round-bottom flask, sodium metal (2.5 g, 108.75 mmol) was refluxed in anhydrous toluene (50 mL) and stirred vigorously to make dispersion. A mixture of trichloromethylsilane (6.4 mL, 54.38 mmol) and trimethoxyvinylsilane (8.3 mL, 54.38 mmol) was added drop wise carefully (Scheme 1). The reaction was highly exothermic. After the addition of monomers, the reaction mixture was refluxed for 12 h. The whole process was carried out in a fume hood and under Nitrogen atmosphere. The reaction mixture was cooled and the suspension obtained was filtered and washed initially with methanol, then with water in a Soxhlet extractor for 24 h, and dried under vacuum. Yield was 47%. Chlorine estimation was done by the modified Volhard's method [4,6,37].

### 2.4. Preparation of hydroxyl substituted PCS

PCS was treated with water to substitute chloro substituent with hydroxyl groups. The reaction was conducted in a round bottom flask; the polymer was refluxed in water for 24 h (Scheme 2). It was cooled and the precipitate obtained was filtered and dried under vacuum.

### 2.5. Preparation of polycarbosilane supported palladium ion (Pd-PCS)

1 g of PCS was stirred in 15 mL of dry toluene for 12 h to swell. Ethanolic solution of palladium acetate (1.35 g, 6 mmol) was added drop wise to the swollen PCS and was stirred for 12 h under reflux condition (Scheme 3). The reaction mixture was cooled, filtered,

Download English Version:

https://daneshyari.com/en/article/64990

Download Persian Version:

https://daneshyari.com/article/64990

Daneshyari.com